UTILIZATION OF DRINKING WATER SLUDGE AND MODIFIED COAL FLY ASH AS ADSORBENTS OF METALS AND METALLOIDS

by

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Abstract

The presence of toxic trace metals and trace elements has drastically increased in recent decades as a consequence of industrialization and a growing demand for natural resources. These toxic metals and elements can be severely harmful to human health and to the environment in general, if they are not properly contained and treated. In the recent years, many papers on the use of low-cost adsorbents to remove toxic metals and metalloids from wastewaters have appeared in the literature. In the category of low-cost adsorbents, coal fly ash or products synthesized from it are commonly studied but drinking water sludge is much less used.

This study is aiming at using waste products to clean the water stream from mine tailing ponds, and developing a new material, which is efficient, and of high performance. Fly ash, sludge and modified fly ash as low-cost adsorbents are presented in this paper and their performance for the removal of metals and metalloids from contaminated water is compared. The adsorption phenomenon could be generally modeled by Langmuir and Freundlich isotherms. Factors that can affect oxyanions (AsO_4^{3-}, SeO_3^{2-}, CrO_4^{2-} and MoO_4^{2-}) adsorption by sludge and fly ash influence the mobility of these inorganic anions in wastewater. This research attempted to compare the adsorption capacities of inorganic anions on sludge and fly ash commonly found in Canada in a tailing pond system. The effects of sample modification, pH and matrix on adsorption were studied; the adsorption kinetics and adsorption capacity if different materials and matrix were investigated. The main goal of this study is to provide some information concerning the use of industrial waste materials as adsorbents for the removal of toxic elements (inorganic anions) from mining wastewater. It is also to determine the chemical mechanisms of toxic elements in water treatment and optimize systematic parameters to be more efficient on the removal of toxic elements from water streams.

Keywords: Toxic elements, Coal fly-ash, Drinking water sludge, Adsorption

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Preface

Industrial wastewater has brought worldwide concern due to contaminated water streams by discharge of toxic elements from industrial processes, such as battery manufacturing, pesticides, printing and photographic industries, metal processing, tanneries and petroleum refining as sources of metal contamination. Metals and metalloids are not biodegradable and can easily accumulate in living organisms as causing toxic and carcinogenic effects and severe diseases to humans and animals.

The current research has been conducted to test the adsorbents (a by-product of an industrial process) for the removal of toxic elements with a focus on anionic forms. Some comparative studies on adsorption properties between different absorbents (e.g. sludge, fly-ash and so on) were also performed under the same experimental conditions.

Due to the low cost and availability of some industrial wastes, much research has been done to investigate applications in wastewater treatment of metal ions, but for elements such as antimony, and molybdenum is very limited.

In the future, there is a need to develop and use low-cost adsorbents with a wide range of metal affinities (possibly through the combination of several waste sorbent materials) that can efficiently remove a variety of inorganic anions from solution from multielement-contaminated wastewaters. Ideally, such adsorbents could be cleaned and re-used.

Chapter 1 Introduction

1.1 Introduction

The presence of toxic trace metals and trace elements has drastically increased in recent decades as a consequence of industrialization and a growing demand for natural resources. These toxic metals and elements can be severely harmful to human health and to the environment in general, if they are not properly contained and treated. In the recent years, many papers on the use of low-cost adsorbents to remove toxic metals and metalloids from wastewaters have appeared in the literature [1-4]. In the category of low-cost adsorbents, coal fly ash or products synthesized from it are commonly studied [5-7] but drinking water sludge is much less studied.

1.2 Research objectives

The main objectives of my thesis were to explore the use of coal fly ash, with or without modification, and drinking water sludge for the removal of metals and metalloids from sulphur containing mine tailing ponds and effluents. The focus on the project was to study the factors controlling the adsorption of selected oxyanions (AsO_4^{3-}, SeO_3^{2-}, CrO_4^{2-}, MoO_4^{2-}) on the selected materials in different aqueous systems, i.e. in deionized water and water from sulphur containing tailing ponds.

1.3 Literature review

This literature review is organized into five sections as follows:

(1) Metals and metalloids
(2) Fly ash—Industrial byproduct adsorbent
(3) DWTS—Industrial byproduct adsorbent
(4) Adsorption isotherms and mechanism
(5) Factors affecting adsorption of metals

1.3.1 Metals and Metalloids

The term Toxic Metals represents a group of metals and metalloids that contaminate or are potentially harmful to the ecosystem. The name toxic metals replaces the confusing term heavy metals [8,9] and it can be used to define metals and metalloids with density and atomic number greater density than 5g/cm³ and 20, such as chromium (Cr), manganese (Mn), cobalt (Co), copper (Cu), zinc (Zn), molybdenum (Mo), mercury (Hg), nickel (Ni), tin (Sn), lead (Pb) and cadmium (Cd). It could be divided into three groups: toxic metals (Hg, Cr, Pb, Zn, Cu, Ni, Cd, As, Co, Sn, etc), precious (such as Pd, Pt, Ag, Au, Ru, etc) and radionuclides (U, Th, Ra, Am, etc.) [10, 11]. In this thesis, the term toxic metals will include metals and metalloids. Toxic metals are used extensively in numerous commercial, industrial and construction applications, and are commonly found in electrical components, house appliances, paints, photographic chemicals, motor vehicles, etc. During industrial process, toxic metals from wastewater and smokestacks are released into the environment. Most of non-commercial substances are normally separated from valuable materials and discarded as waste. These waste materials can release metals into the environment through oxidation, weathering and solubilization.

1.3.1.1 Toxic metals in the environment

Metals are not only produced and introduced into the environment by human activities, but they can also originate from natural processes, such as weathering, volcanoes and geothermal activities. Since the amount of metals released from human activities is increasing every year, it has brought a worldwide attention. Their toxicity and bioaccumulation capacity pose a serious threat to human's and animal's lives. Metals are not degradable, and metals originating from natural process are less toxic or nontoxic because they are usually present at very low concentrations. However, industrial processes and human activities can lead to high concentrations of toxic metals hence technologies aiming at removing toxic metals from contaminated environment become very important.

1.3.1.1.1 Arsenic

Arsenic is a natural element that is present in the Earth's crust. It has been characterized as toxic and carcinogenic element. In nature, arsenic exits in a large variety of compounds. In the ocean, arsenic is commonly identified as a terrigenous deposit, i.e. from surface runoffs and subsurface sediments [12]. Furthermore, arsenic is mainly introduced by human activities such as mining and smelting, pharmaceuticals, paper pulp and pesticides production.

Human and animal get exposure to arsenic from drinking water, food, soil and air. The common forms of arsenic include inorganic and organic species: arsenite (As^{III}), arsenate (As^{V}), monomethyl arsenic acid (MMA^{V}), dimethyl arsenic acid (DMA^{V}), arsenobetaine (AsB), arsenocholine (AsC), arseni**c** sugars and lipids. The transformations between each form highly depend on the chemical and biochemical conditions of the system. Inorganic forms of arsenic are more toxic than organic ones. For example, the toxic levels of monomethyl arsenate MMA ($CH_3AsO(OH)_2$) and dimethyl arsenate DMA ($(CH_3)_2AsO(OH)$) are only 1/400 of inorganic arsenic [13]. Inorganic arsenic is known as strong carcinogen and MMA^{V} and DMA^{V} are defined as potential carcinogens [14]. However, some organic arsenic are considered non-toxic, such as arsenobetaine ($(CH_3)_3As^{+}CH_2COO^{-}$) and arsenocholine ($(CH_3)_3As^{+}CH_2CH_2OH$). They cannot be digested or adsorbed by humans or animals. The toxicity of arsenic compounds is as following: $AsH>As^{III}>As^{V}>MMA^{V}>DMA^{V}$ [14]. The toxicity of arsenic is therefore strongly depending on valence and its chemical forms. The strong affinity of arsenic species to adsorb on oxyhydroxide surfaces (aluminum, iron, manganese, etc.) is well known and has been exploited in the treatment of drinking and wastewaters [2, 16].

1.3.1.1.2 Selenium

Selenium is an essential element to humans and animals but it becomes toxic at a higher level. That is when it is at low concentration (intake level is lower than 0.4 mg day^{-1}), it is used as antioxidant. It can protect cells from damage. There are four oxidations states of selenium: -II, 0, IV, and VI. The toxicity of selenium depends also on

its oxidation states and chemical forms. In natural systems, selenide (Se^{2-}), elemental Se (Se^{0}), and selenite (SeO_3^{2-}) can be transformed into each other under certain conditions of pH, redox potential and temperature[17]. As many other chalcophile elements, selenium can be released to the environment through mining and smelting activities involving sulphidic ores [18, 19].

1.3.1.1.3 Chromium

In the environment, there are two main oxidation states of chromium: Cr(III) and hexavalent chromium Cr(VI)which presents as the oxyanion CrO_4^{2-}. Hexavalent chromium salts such as chromate and dichromate are powerful oxidants. They are commonly used as pigments for photography, inks, plastics, dyes and pyrotechnics. Chromate can be also used for stainless steel production, textile dyes, wood preservation, leather tanning and anti-corrosion coatings [20]. Humans are exposed to hexavalent chromium mainly from food and water coming from soil and aquatic environments. Due to its strong mobility and availability, humans and animals can easily absorb it. On the other hand, chromium oxide as Cr(III) is rather immobile and innocuous, and is an essential element for metabolism. Various technologies are presented in the literature to remove chromium from wastewaters [21].

1.3.1.1.4 Copper

Copper is mainly used in electrical and electroplating industries. Copper is an essential element for life at low level and it functions as biological electron transporter and plays an important role in various enzymes. When the concentration of copper is high, it becomes toxic to living organisms. It can be deposited in brain, skin, liver, pancreas and myocardium [22]. Copper usually exits in the environment as oxides and sulphides. High doses of copper can cause anemia, liver and kidney failure, and stomach and intestinal irritation. For example, the Wilson's disease can be triggered by high doses of copper, which leads to brain and liver damage. There is no cure for Wilson's disease. Human are exposed to copper in drinking water from copper pipes. The safe level of copper is proposed to be at 1.3 mg/L according to the US Environmental Protection Agency. The common oxidation states of copper are less stable copper (I) state Cu^{+}, and

the more stable copper (II) Cu^{2+} [23].Copper pollution can be due to mining, printed circuits, fiber production, water pipe corrosion, metal plating industries [24], fertilizers and fungicidal sprays and animal waste. Copper can also be found in packaging containers for food, water and soft drinks [14]. In fact, the number of workers who are sick from copper exposure in mining companies increases every year. Most of them suffer from lung cancer [13].

1.3.1.1.5 Nickel

The production of nickel is mainly associated to stainless steel, steel alloys, and electroplating. Its minor sources are from paper mills, fertilizers, petroleum refining and the production of colored glasses. Nickel is a trace metal, which exits in soil, air, water, and biosphere. The average concentration of nickel present in Earth's crust is 0.008%. The prevalent ionic Ni^{2+} is considered non toxic at low concentrations due to the low adsorption from food and water by humans. Exposure to soluble nickel compounds can cause nasal cavity and lung cancer by inhalation, ingestion and eye or skin contact [25].The presence of nickel (and copper) in mine effluents around Sudbury is related to its extraction from the underground deposit.

1.3.1.1.6 Molybdenum

Molybdenum can exist in many oxidation states (2, 3, 4, 5, 6) and most Mo compounds have low solubility in water. Under oxidizing conditions like those prevailing in mine waters, the most oxidizing form and soluble form molybdate MoO_4^{2-} will normally dominate. Molybdenum compounds are used in the industry for high-pressure and high-temperature applications as pigments and catalysts. Excessive amounts of molybdenum can irritate the eyes and skin, dizziness, chest pain, cough and other symptoms. Molybdenum at low concentration is an essential element for human beings and animals, it helps to metabolize carbohydrate and detoxify sulfite. Based on the health effects from chronic exposure to Mo, the guideline value for Mo in drinking water was recently modified to 0.07 mg/L [26]. Human exposure to molybdenum for a long term, it will cause liver dysfunction. Also, other cases show the molybdenum lead to joint pains in hands, feet and articulation deformities in some factories in Armenia.

Table 1 Type of metals and effects of human beings

Metal	Major source	Toxic effects	References
Lead	Mining, paint, pigments, electroplating, manufacturing of batteries, burning of coal	Anemia, brain damage, anorexia, malaise, loss of appetite, liver, kidney, gastrointestinal damage, mental retardation in children	[27,28]
Copper	Plastic, copper polishing, paint, printing operations	Neurotoxicity, and acute toxicity, dizziness, diarrhea	[29]
Cadmium	Plastic, welding, pesticide, fertilizer, mining, refining	Kidney damage, bronchitis, Gastrointestinal disorder, bone marrow, cancer, lung insufficiency, hypertension, Itai-Itai disease, weight loss	[30,31]
Zinc	Mining, refineries, brass manufacturing, plumping	Causes short term ”metal- fume fever”, gastrointestinal distress	[32]
Mercury	Batteries, paper industry, paint industries, mining	Damage to nervous system, protoplasm poisoning, corrosive to skin, eyes, muscles, dermatitis, kidney damage	[33]
Nickel	Porcelain enameling, non-ferrous metal, paint formulation, electroplating	Chronic bronchitis, reduced lung function, lung cancer,	[25]
Arsenic	Smelting, mining, rock sedimentation, pesticides,	Bronchitis, dermatitis, bone marrow depression, haemolysis, hepatomegaly.	[34]
Chromium	Textile, dyeing, paints and pigments, steel fabrication	Carcinogenic, mutagenic, teratogenecity, epigastria pain nausea, vomiting, severe diarrhea, producing lung tumors	[35]
Molybdenum	Semiconductor ,optoelectronics, thin film transistor liquid crystal display	Affect male reproductive health, irritate the eyes, skin, contacts pneumoconiosis disease, whole body fatigue, dizziness, chest pain, cough	[26]

1.3.1.2 Regulatory issues (Water quality standards)

Metal pollution from human activities is one of the most important environmental issues in the world. Most of toxic metal ions are threat to humans and animals, and some of their effects on humans are listed in **Table 1**. In order to protect living organisms, the efficient removal of toxic metals from the water stream needs to be carefully studied. In fact, industrial effluents are a major source of this pollution, which is caused by corrosion of water pipes, waste dumping, mining activities, surface finishing, fuel producing, fertilizers, pesticides, electroplating and electrolysis, etc.[36]. Because of the non-degradable property of metal, removing and recovering them from industrial effluent streams are the two main goals.

Some metals are essential elements to humans and animals when they are at low concentration [37,38]. The United States Food and Drug Administration (FDA) proposed a standard list of these essential elements in drinking water since drinking water is the main pathway for living organisms expose to them. For those are not essential element, FDA also indicates the concentration of these elements at non-harmful level, such as arsenic. The limits and the healthy impact of metal contaminant are shown in **Table 2**[39–41].

Table 2 Permissible limits and health effects of various toxic metals [39–41]

Metal contaminant	Permissible limits for industrial effluent discharge(in mg/L)		Permissible limits for drinking water(mg/L)			Health hazards
	Canada std	WHO	WHO	USEPA	EU	
Arsenic	0.010	_	0.01	0.01	0.01	Carcinogenic, producing liver tumors and shin and gastrointestinal effects
Mercury	0.001	_	0.001	0.002	0.001	Corrosive skin, eyes, and muscle membrane, dermatitis, anorexia, kidney damage, and severe muscle pain
Cadmium	0.005	0.1	0.003	0.005	0.005	Carcinogenic, cause lung fibrosis, dyspnoea, and weight loss
Lead	0.010	0.1	0.01	0.015	0.01	Suspected carcinogen, loss of appetite, anemia, muscle and joint pains, diminishing IQ, cause kidney problem, and high blood pressure
Chromium	0.05	_	0.05	0.1	0.05	Suspected human carcinogen, producing lung tumors, and allergic dermatitis
Nickel		_	0.02	0.1	0.02	Causes chronic bronchitis, reduced lung function, cancer of lungs, and nasal sinus
Zinc	≤5.0	5.0~15.0	3.0	5.0	-	Causes short-term illness called “metal fume fever” and restlessness
Copper	≤1.0	0.05~1.5	2.0	1.3	2.0	Long term exposure causes irritation of nose, mouth, and eyes, headache, stomachache, dizziness, and diarrhea
Manganese	≤0.05		0.5	0.05	0.05	Excess amounts toxic, and causes growth retardation, fever, sexual impotence, muscles fatigue, eye blindness.
Selenium	0.05		0.003	_	0.003	Chronic selenosis symptoms in humans following exposure to high levels. Other: Hair loss, tooth decay, weakened nails and nervous system disturbances at extremely high levels of exposure

Note : USEPA: U.S. Environmental Protection Agency; WHO: World Health Organization

1.3.1.3 Removal of toxic metal ions from wastewater

There are three major categories of technologies for removing toxic metal ions from wastewater: (1) biological, (2) chemical and (3) physical. Most of these techniques are used for surface water and groundwater. At the present time, there is not a single technique capable of removing large amount of toxic metal contamination from effluents. Usually, the most efficient treatment has to combine different processes in the most economical way.

The biodegradation treatment is in fact the most economical alternative, when it is compared to physical and chemical processes. Biodegradation methods are mainly used for organic pollutants, such as applying bacteria, yeasts, algae and fungi to the industrial effluents. Metals are not degradable and cannot be efficiently eliminated [42]. Chemical treatments are often expensive and create a disposal problem, resulting from flocculation combined with floatation and filtration, precipitation, electro-floatation, conventional oxidation, methods by oxidizing agents (ozone), irradiation or electrochemical process. Physical treatments require less operation area and disposal of waste, such as membrane-filtration process, reverse osmosis, electrodialysis, etc. However, they are more expensive due to constant replacement of the devices and short lifetime. Therefore, it is important to develop techniques, which are inexpensive and applied at large scale of effluents to achieve the desired water quality. Liquid-phase adsorption is one of the most common treatments that have been applied in wastewater. Adsorption depends on the presence of unbalanced forces at the surface of liquid or solid phase. It requires efficient adsorbents, which can be waste products, such as drinking water sludge and fly ash. Depending on the chemical and physical properties of used adsorbents, most of them do not require pre-treatment. During the adsorption process, there are not harmful substances being formed. The advantages and disadvantages of various water treatments have been shown in **Table 3**[43].

Table 3 Current treatment technologies for metals removal involving physical and/or chemical processes [43]

Physical and/or chemical methods	Advantages	Disadvantages
Oxidation	Rapid process for toxic pollutants removal	High energy costs and formation of by-products
Ion exchange	Good removal of a wide range of heavy metals	Absorbent requires regeneration or disposal
Membrane filtration technologies	Good removal of heavy metals	Concentrated sludge production. expensive
Adsorption	Flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants	Adsorbents requires regeneration
Coagulation/flocculation	Economically feasible	High sludge production and formation of large particles
Electrochemical treatment	Rapid process and effective for certain metal ions	High energy costs and formation of by-products
Ozonation	Applied in gaseous state: alteration of volume	Sort half life
Photochemical	No sludge production	Formation of by-products
Irradiation	Effective at lab scale	Required a lot of dissolved O_2
Electrokinetic coagulation	Economically feasible	High sludge production
Fenton's reagents	Effective and capable of treating variety of wastes and no energy input necessary to activate hydrogen peroxide	Sludge generation
Biological treatment	Feasible in removing some metals	Technology yet to be established and commercialized

1.3.1.4 Industrial wastes as an adsorbent for removal of toxic metals

The removal toxic metals from water stream can be carried out by chemical precipitation, solvent extraction, ion-exchange and adsorption. Among these industrial processes, the adsorption is considered effective and low-cost.

Some industrial wastes represent potential adsorbents for removing metals from wastewater since they are very often locally available and inexpensive [42]. In order to improve adsorption, a waste material requires showing high adsorption capacity in a certain pH range. Industrial wastes include fly ash, blast furnace sludge, waste slurry, lignine and red mud and water sludge, among others. These have been studied as potential adsorbents for the removal of toxic metals and metalloids.

1.3.2 Coal fly ash—Industrial byproduct adsorbent

Coal fly ash is an anthropogenic material obtained from coal combustion, which is one of the main sources for energy production in the world. Coal consumption is predicted to increase by 49% from 2006 to 2030 [43]. It has become a global environmental problem due to the large quantities of fly ash being produced. In fact, coal fly ash is considered as a mining waste because it contains potential toxic elements (e.g. Cd, Cr, Ni, Pb) and organic compounds (e.g. polychlorinated biphenyls, polycyclic aromatic hydrocarbons). Disposed coal fly as on lands is likely to contaminate soil. Therefore, scientists are trying to develop practicable methods for reusing coal fly ash.

Coal fly ash is divided into two types: coarse bottom ash and fine fly ash. Both types are mechanically removed during airflow to the bottom of the boiler [44,45]. The term of fly ash is usually referred to particles that are captured from flue gas and collected by electrostatic or mechanical precipitation. Every year, 20% of coal fly ash generated is used in concrete production, road base construction, soil amendment, zeolite synthesis; however, the 80% of coal fly ash is discharged into ash ponds, lagoons or landfills, where it could potentially contaminate the environment [46]. From 2010 to 2014, some scientists have proposed some possible applications of utilizing coal fly ash from perspective of soil amelioration and mine reclamation [47-49], alumina and cenosphere recovery[50,51], adsorbents for mercury removal, CO_2 capture and wastewater treatment [52,53], among others. However, they did not mention the generation of coal fly ash worldwide. This thesis will discuss current utilization of coal fly ash and identifying some promising applications.

1.3.2.1 Structure of fly ash

The major components of coal fly ash are silica (SiO_2), alumina (Al_2O_3) and iron oxides (Fe_2O_3). The pigment (color) of fly ash is mainly dependent on the amount of iron oxides and carbon contents. The presence of high amount of Fe_2O_3 gives coal fly ash a dark color [54]. In fly ash, there are also varying amounts of carbon, calcium, magnesium and sulphur (**Table 4**). An empirical formula of fly ash has been proposed as [55]:

$Si_{1.0}Al_{0.45}Ca_{0.51}Na_{0.047}Fe_{0.039}Mg_{0.020}K_{0.013}Ti_{0.011}$.

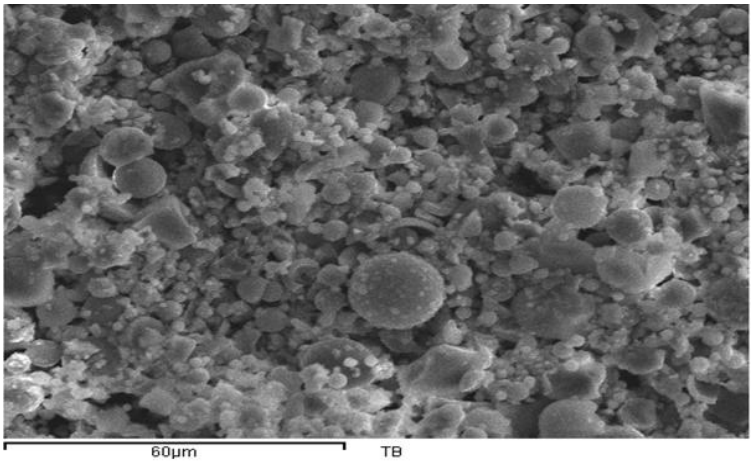

Figure 1 A typical SEM image of coal fly ash obtained from Thunder Bay Power Generation Plant

In general, fly ash has a hydrophilic surface and porous structure. **Figure 1** shows the typical SEM images of fly ash. The observation reveals that fly ash particles (with an average diameter <10 µm) [56] are predominantly spherical (0.01~100 µm) [57] in shape and consist of irregular-shaped debris and porous un-burnt carbon. The irregular fragments are mainly made of un-burnt carbon, anhydrate and calcite.

Table 4 Elemental composition of fly ash (%wt) [58] in Canada

Composition	**%wt**
SiO_2	47.00
Al_2O_3	16.59
Fe_2O_3	20.13
CaO	8.70
MaO	3.40
Na_2O or K_2O	1.14
SO_2	1.37
TiO_2	0.61
P_2O_3	0.08
loss on ignition(LOI)	-

1.3.2.2 Physical and chemical properties of coal fly ash

The physical and chemical properties of coal fly ash are dependent on combustion conditions, collector setup, boiler types and gas emission control system[59]. In order to determine the valuable of coal fly ash in environmental improvement, studying its physical and chemical properties is very important. **Table 5** shows the main physical and chemical properties of fly ash.

Table 5 Physical characteristics of fly ash

Specific gravity g/cm^3	Particle size μm	Surface area cm^3/g	pH
1.8~2.6	0.01~100	2500 ~4000	4.5~13.25

Coal fly ash is comprised of fine, spherical and hollow spheres particles, so it can be applied as cleaning adsorbents for metals and elements (Cu, Pb, Cd, Ni, Zn, Cr, Hg, As, Cs, fluoride and boron). In 1991, Alonso and Wesche discovered that coal fly ash particles have large cenospheres (inert, hollow spheres made largely of silica and alumina and filled with air or inert gas) and plerospheres (which have their cavities filled by finer particles of ash and other materials) with surface area from 2500 to 4000 cm^3/ g, as measured by the Blaime method [54]. Therefore, coal fly ash has a great adsorption capacity.

The chemical characteristics of coal fly ash are influenced by geological factors, such as coal deposits and different operating conditions at power plants. Thus, each coal fly ash has its own chemical characteristics in different areas. For example, the pH of coal fly ash varies from 4.5 to 13.25, due to the different amount of sulphur and CaO contents of the parent coal [60].

1.3.2.3 Hazards

The environmental impact of coal fly ash has been fully recognized. Most industries dump fly ash on open lands. In some countries, coal fly ash is considered as a solid waste instead of a hazardous waste. However, the accumulation of disposal of fly ash leads to the clogging of natural drainage system and the contamination of groundwater, which are threat to living organisms and the environment. Since fly ash particles are very fine, they are easily

suspended in air and inhaled by animal and humans. For humans, chronic exposure to fly ash can cause irritation of skin, nose, throat and respiratory tract.

Coal contains various trace metals; however, their concentrations are 4-10 times higher in fly ash than in parent coal after combustion. These trace metals can possibly be easily leached out from the surface of fly ash particles by the interaction of with water in landfills. Some of trace elements are water-soluble that can contaminate the aqueous environment [61,62]. In 2012, scientists discovered some trace elements in fly ash are potential threat to the environment at low levels, such as V, Cr, Ni, Cd and Pb. Some trace elements can be leached easily to the atmosphere, soil and water, such as As, Zn, Pb, Ni, Mo, Cr and Cu[63]. However, the combustion of coal at high temperatures very likely favors the elimination of volatile elements and some of their salts.

1.3.2.4 Comprehensive applications

Fly ash is an abundant waste material from thermal power plants. Currently, scientists are developing effective methods that are designed to re-use fly ash. One of the effective methods is to use coal fly ash as cleaning adsorbents for gas and water treatment. Recycling coal fly ash is a significant environment and economic benefit. The average of global utilization of fly ash is less than 25% and a large percentage of disposing of fly ash has been dumping into landfills, which could be the potential hazards to environment [64] . Based on previous research, the current utilization of fly ash is illustrated in **Figure 2**.

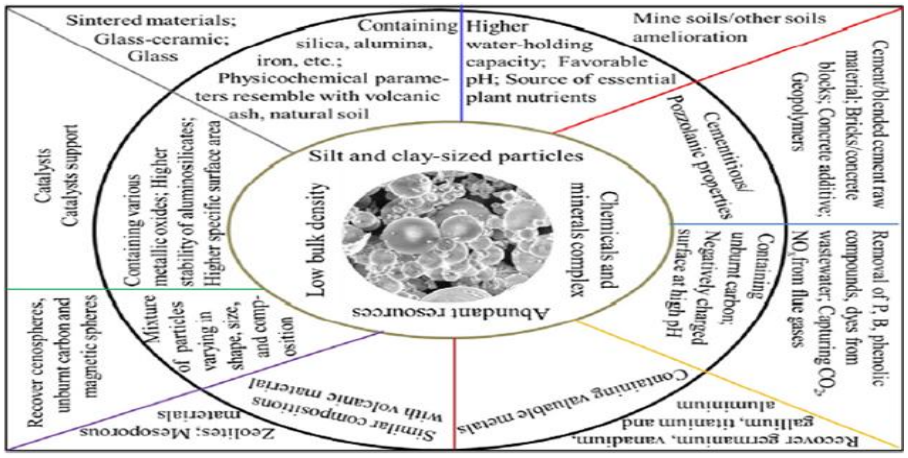

Figure 2 Current applications of coal fly ash [65]

1.3.2.5 Adsorption of metals on fly ash

The adsorption performance of fly ash is mainly dependent on the physical and chemical properties of the material, such as particle size, surface area, pH, solid/liquid ratio and the concentrations of trace elements. In fact, the alkaline nature of fly ash make it a good adsorbent for Ni, Cu, Pb, Cd and Hg. Unmodified fly ash generally has usually low adsorption performance due to the small pore size and surface area [42,47, 66].

For example, the removal of hexavalent chromium by homogeneous mixture of fly ash and wollastonite (1:1) has been studied. The critical factors to consider are pH of the matrices, adsorbent type, Cr(VI) concentration and contact time on the selectivity and sensitivity of the removal process[67]. In some studies, they compared the adsorption performance of fly ash with other low-cost adsorbents (sludge, saw dust, neem bark). They found that sludge was the most effect adsorbents for Cr(VI) from an aqueous solution. The results suggest that the adsorption includes two stages: 1) initial stage of boundary layer diffusion, which is due to unbalanced forces of internal and external nature; 2) later stage of the rate determining step, which is caused by intra-particle diffusion[68].

There are also studies describing the utilization of fly ash to remove Cu(II). The removal efficiency is highly depending on the pH and physical and chemical characteristics of the fly ash [69]. The results of kinetics adsorption showed that the carbon fraction in fly ash is also one of the critical factors for removing Cu(II) from aqueous solutions. The specific adsorption capacities of carbon in fly ash ranged from 2.2 to 2.8 mg Cu/g carbon [70]. Also, it is indicated that at high pH level, the removal efficiency of ions such as Cu (II) and Pb(II) got improved[71]. However, chemical precipitation should be considered as one of the possibilities of removing ions in this case.

1.3.3 Drinking water sludge—Industrial byproduct adsorbent

Drinking water sludge is a major component of water treatment residues from drinking water treatment facilities. During the drinking water treatment, either aluminum or iron salts will be applied into the water as a coagulation-flocculation agent, which allows particles to form into large masses and then be trapped in the filter [72]. Drinking water sludge contains large amount of precipitated hydroxides (alum-based or ferric-

based. In the sludge, there are various other substances, such as activated carbon, humic substances and long-chain polymers [73]. From Okuda's report, there is 10,000 tons of daily sludge produced from water treatments in European countries including Ireland, Germany, Netherlands and so on [74]. In fact, United States takes up 72.6% of the global sludge production. Utilizing drinking water sludge has brought global concerns since the amount of daily water sludge production increases. Considering that the adsorption capacity of drinking water sludge has not generally reached saturation treating water from wells and water bodies, it can still be used to purify more contaminated waters such as industrial and mining effluents.

1.3.3.1 Origin of drinking water sludge

In order to use water for human consumption, it requires removing undesirable chemical and biological contaminants from raw water. The water purification process includes precipitation and filtration that settle the particles to form large masses of the water material and then reduce the concentration of chemical and biological contaminants by trapping in a clarifier. These particulates material settled in a filter to form sludge. These suspended particles are referred to as drinking water sludge, which is a diluted solid mixture liquid [43].

The water sludge contains large amount of organic or inorganic materials, which depends on the specific water treatment from different water facilities. The treatment includes oxidation, coagulation and flocculation that allow the particles to be suspended and separated from the drinking water. The pH of drinking water sludge is usually slightly acidic due to flocculation and coagulation agents added to the process.

1.3.3.2 Dinking water sludge characteristics

Drinking water sludge is a waste material generated from removing contaminants from raw water in the purification process. The water sludge is accumulated on the granular medium after adding the aluminum or ferric salts in which causes precipitation in raw water. Generally, the process of water treatment includes[75]:

a) naturally-occurring colloidal and other particulate matter (*e.g.* silt, clay, algæ);
b) natural organic matter (NOM) dissolved in raw water (*e.g.* humic acids, fulvic acids);
c) water treatment chemicals precipitation;
d) precipitates of inorganic materials dissolved in the raw water (*e.g.* iron, manganese); and
e) granular medium flushed out during backwashing.

However, water sludges can differ based on specific water treatment process. This general process summarizes most of industrial wastewater treatment process.

Because of the water treatment, drinking water sludge contains high moisture between 70% and 80% in volume. That sludge contains a large amount of hydrophilic solids that leads it to be voluminous in nature. This hydrophilic solid contact with water and contribute to the volume of moisture content in sludge. Sludge is classified as a muddy or slurry mass precipitate from drinking water treatment. This characteristic of sludge limits the possibilities of reuse. The chemical compositions of water sludge are as varied as the season of year, and the quality and quantity of effluents discharged by the wastewater treatment plants. Most wastewater treatments combine mechanical and biological treatments aiming at dissolving organic matter, settling the large masses of particles, reducing the concentration of biological and chemical containments (viruses, bacteria and inorganic matter) from raw water, and then meeting the standards of water quality for human consumption. Microorganisms can absorb the inorganic matter from water sludge, so that insoluble nitrogen and phosphorus compounds are removed.

Sludge can be divided into two phases: solid and liquid. The solid phase includes organic and inorganic compounds, and the liquid phase contains water and water-soluble matter. The component of water sludge is shown in **Figure 3**[76]. Toxic metals are accumulated from water purification and exposure to the environment and humans, which can be hazardous.

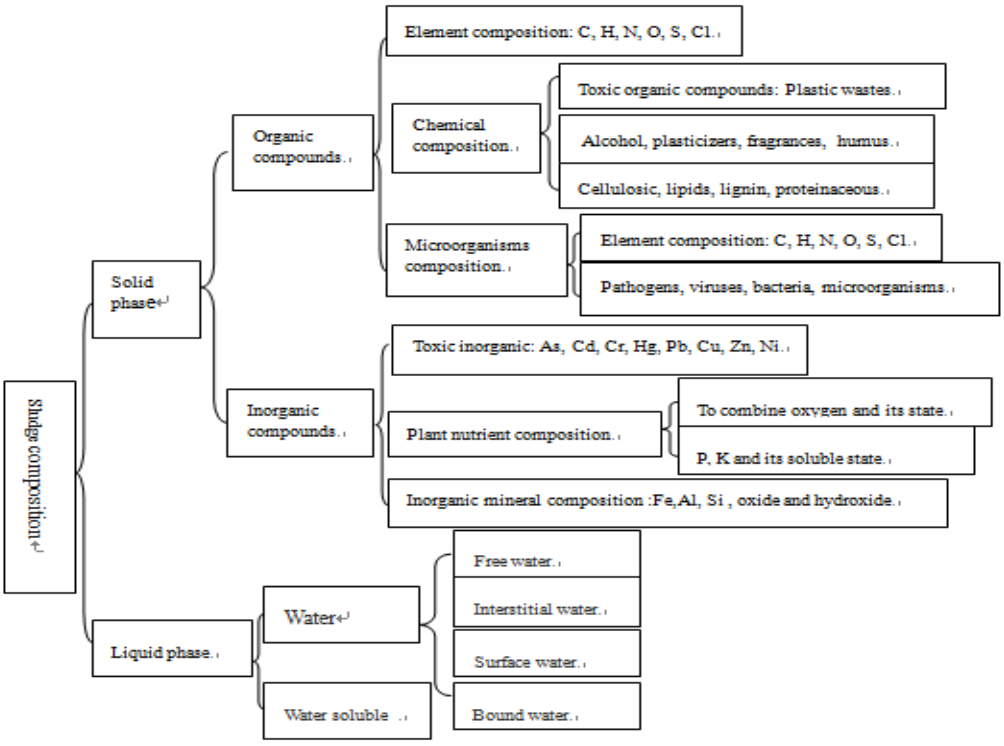

Figure 3 The description of the basic compositions of the municipal sludge

1.3.3.3 Disposal and reuse of water sludge

Drinking water treatment sludge can potentially become a global environmental concern due the large quantities of water sludge production from the water treatment facilities. Therefore, it is important to study the nature of water sludge and develop applications for reusing it. According to Makris and Harris in 2005 [77], drinking water sludge could be used as plant growth medium, depending on the high organic matter and nutrient contents, by spreading it below the soil surface of agricultural lands.

Sludge can be used as a fertilizer due to the high contents of organic matter for soil conditions [78]. Since water sludge is generally free of charge from water treatment plants, the application of using sludge as fertilizer is low-cost and prevents environmental pollution. However, it also triggers the potential contamination of surface water, groundwater, soil, and crops, due to the hazardous contaminants of sludge, such as dioxins, pathogens, polychlorinated biphenyls, pesticides, and especially toxic metals,

including cadmium, chromium, cobalt, copper, iron, manganese, mercury, molybdenum, nickel, silver and zinc. In order to purify large amount of raw water, adding Al or Fe salts is the most common and economic water treatment. It is used to remove particles and organic matter [79,80]. After the coagulation-flocculation process, water sludge must be disposed in landfill or into the ocean. Developing applications to reuse water sludge is an important approach that is promoting the recycling of valuable materials and reducing the waste residues.

There are two main concerns of reusing drinking water sludge; they are the chemical safety and the biostability. Sludge can release undesirable organic (humic-like and protein-like substances) and inorganic (phosphorus, arsenate, boron, and metals [81-84] pollutants. Therefore, a pretreatment for sludge can be necessary. The common pretreatments are divided into two methods:

1) chemical method (i.e., acid, alkaline and ozone/ultrasound treatment)
2) physical method (i.e., thermal and mechanical treatment), and biological method (enzyme treatment)

In fact, the ultrasound treatment is one of the most commonly used for water sludge due to its high performance and low-cost. This treatment is used to increase the surface area of particles and removing the toxic substances by an oxidizing process [83-87]. However, such pretreatments are only capable of treating small amounts of drinking water sludge.

1.3.3.4 Adsorption of metals on drinking water sludge

Drinking water sludge can be used as an adsorbent for many purposes. For example, drinking water sludge was used to remove Cd(II) and Ni(II) from aqueous solution through chemical pyrolysis [88]. The adsorption capacity was estimated at 16 and 9 mg/g for Cd(II) and Ni(II), respectively, based on the Langmuir isotherm model. From the results, it was proposed that the adsorption was caused by ion exchange.

In another case, distillery sludge was applied to remove chromium(VI) from aqueous and industrial effluents. The adsorption capacity was calculated at 5.7 mg/g. It also showed that 82% of hexavalent chromium was removed, which means that sludge can be used as adsorbents to meet economical product requirements for metal remediation from water and wastewater [89] .

In another study, different conditions sludge (5-20 days ages) was used to adsorb Cd and Ni. The study suggests that different sludges have various adsorption sites for each element. Cd was mainly adsorbed on extracellular polymer slimes and Ni was on capsular polymers and cellular walls [90].

1.3.4 Adsorption isotherms and mechanisms

Adsorption is one of the most efficient processes to control the mobility and transport of pollutants in the aquatic environment and reduce the concentration of inorganic and organic contaminants from drinking and waste water. In this case, sorption is the process that describes one inorganic or organic component moves from one phase to another via some boundary [91]. During the process, metal ions will be captured on the particle surfaces. Sorption is also the process of a metal ion going from aquatic environment to particle solid surfaces, which could combine with many processes, such as adsorption and surface precipitation [92 ,93].

1.3.4.1 Chemisorption

Depending on the types of interactions occurring at the contact surface, phenomena can be divided into two pathways: chemisorption and physisoption. In chemisorption, a chemical bound is formed between the adsorbent and the adsorbate whereas physisoption is mainly referring to *van der Waals*' type interaction between the adsorbate and the adsorbent [94, 95]. In order to distinguish between chemisorption and physisoption in the process, heat and reversibility of adsorption and thickness of the adsorbed layer need to be identified [94-97].

1.3.4.2 Adsorption isotherms

Determining the adsorption phenomena is described by adsorption isotherms. That is the amount of adsorbate being adsorbed by a certain amount of adsorbent under thermodynamically equilibrium conditions at a constant temperature. The most commonly isotherm models for adsorption are (1) the Langmuir isotherm and (2) the Freundlich isotherm [96, 98, 99].

Langmuir isotherm is a basic adsorption model, which is used to express when the monolayer adsorption is formed on a homogeneous surface. The Langmuir equation is usually the first step calculation for studying the chemisorption [94, 96]. On the other hand, Freundlich is used to describe a more complex adsorption phenomenon, in which multiple-layer adsorption is formed on a heterogeneous surface. However, not many studies have been done about the effects of surface heterogeneity, the theory of heterogeneous surfaces being still uncompleted. Due to the complicated water treatment process, adsorption is usually assumed as a homogeneous phenomenon in most of cases. Therefore, the Langmuir and Freundlich isotherm are the most useful equations[96,99].

The mechanisms of metal ion adsorption include electrostatic attraction, ion-exchange, adsorption–precipitation, hydrogen bonding, and chemical interaction. In fact, the chemical interaction has been studied as the major adsorption mechanism between metal ions and surface functional groups of water material. Also, it is well known that adsorption for metal cations is more effective in an alkaline environment (pH greater than 7). However, the adsorption is a complicated process that combines adsorbents and adsorbates. When adding adsorbent into the solution of adsorbates, the pH can be difficult to control in a set range; that increases the difficulties of determining the mechanism of metal adsorption. According to Dushina and Aleskovaski [100], the first step of adsorption for metal ions by various calcium silicate materials (such as slag) is ion exchange. Metal silicates can be formed on the surface of the material. For example, Lopze et al. [101] evaluated the adsorption capacity of blast furnace sludge, and applied it to remove Pb (II) from aqueous solutions. Their results showed that the adsorption of

Pb(II) was attributable to ion exchange with calcium on surface and precipitation on $Al(OH)_3$ and SiO_2[102].

1.3.5 Factors affecting adsorption of toxic metals

1.3.5.1 Effect of contact time and initial concentration

There are many factors affecting the adsorption performance of metals on a surface, such as the initial metal concentration, the pH of aqueous matrix, the temperature and the contact time, the particle size and the ionic strength of the solution. In fact, the initial concentration of adsorbates strongly affects the adsorption capacity of the adsorbent (such as waste water sludge, fly ash and other industrial wastes). The adsorption capacity increased as initial concentrations of adsorbent are increasing. The initial concentration gradient contributes to the metal transferring from the aqueous phase to the solid phase. Also, the contact time for each adsorbent is mainly depending on the nature of the adsorbent. Thus, the adsorption by clarified sludge and rice husk ash reached equilibrium when the contact time was 3 hours. For activated alumina and neem bark, the contact time needed to reach equilibrium was established at 4 hours. The results are similar to those reported by Zheng et al. [103]. Nickel (II) adsorption equilibrium of waste tea was established when the contact time was 2hours. The initial concentrations of Ni (II) varied from 30 to 300mg/L. When the initial concentration was 100mg/L, 8.12mg/g of Ni was adsorbed at 30min, and 8.24mg/g at 120min. When the initial concentration of Ni (II) increased from 50 to 300 mg/L, the adsorption capacity of waste tea enhanced from 4.413 to 14.04 mg/g [104].

1.3.5.2 Effect of pH

The pH of surface sites and aqueous environment is one the **most critical factors** for adsorption. In general, the adsorption of metals that are positively charged in solution will increase when the aqueous is more alkaline; for others that are negatively charged, adsorption will be enhanced when the aqueous gets more acidic.

1.3.5.3 Effect of particle size

Intra-particle diffusion studies show that the particle size of the waste materials strongly influences the adsorption rate. On one hand, decreasing the size of the particle would limit the adsorption opportunity at the outer surface that becomes smaller. There is also a possibility of intra-particle diffusion from the outer surface in the pores. Such diffusion is strongly affected by the external surface area of the particles. That means that larger particles show a decrease of their adsorption capacity. On the other hand, if we consider the same mass of material where particles would be much smaller in size, it would imply a much larger surface area and a much larger adsorption capacity compared to the same mass of larger particles. Amarasinghe and Williams [105] studied the effect of particle size of tea waste on the adsorption for metals. The results showed that when the average particle sizes of tea waste were 1250, 925 and 575μm, the corresponding removal percentage of Cu(II) were 41%, 53% and 57%, respectively. Another study using three different particle sizes(100~150, 200~250, and 300~350μm) at pH 6.0 for l0g/L of lead and pH 5.0 for 10g/L of chromium, with a contact time for lead of 80min, and 60 min for chromium showed that the adsorption of lead and chromium were 88.0%, 95.0% and 99.9%, respectively [106]. That is the larger surface area corresponding to higher adsorption capacity.

1.3.5.4 Effect of ionic strength

Knowing the ionic strength is useful to understand the affinity between the adsorbent and adsorbate, since it also affects the aqueous phase equilibrium. Increasing the ionic strength of the aqueous solution leads to a decrease of the rate of adsorption. Based on the surface chemistry theory, an increase of the ionic strength induced by other ions will also increase the competition for binding sites of particles and make it more difficult for metals to bind. For example, the percentage of Cr(VI) adsorbed on red mud decreased with higher concentration of additional ions. The affinity order for adsorption on activated red mud was $PO_4^{3-} > SO_4^{2-} > NO_3^-$ [107].There was another ionic strength study was done by Weng and Huang [108]. Their result showed, lower ionic strength corresponding to a higher Zn(II) removal percentage.

Chapter 2 Experimental methodology

The purpose of the study was to investigate the applicability of selected low cost materials in contaminant removal from wastewaters in the mining environment, with an emphasis on oxyanions such as AsO_4^{3-}, SeO_3^{2-}, CrO_4^{2-}, MoO_4^{2-}, although Ni^{2+} and Cu^{2+} adsorption behaviors were briefly investigated at the beginning. A special attention has been given on low energy consumption during the material modification, which means that modification of material under low temperature and with reusable alkaline liquor (NaOH).

2.1 Sample preparation

Adsorbents

2.1.1 Fly ash sample (TB)

The original fly ash sample (**TB**) was obtained from the Thunder Bay Power Generation Plant located in Ontario, Canada. The sample was oven dried at 50°C and homogenized with a ball mill for 5 min.

2.1.2 Fly-ash treatment under low temperature (TBFZ3)

To generate a modified material, 50.00g of fly-ash was placed in a 1000 mL high density polyethylene (HDPE) bottle and a 500mL aliquot of 2.0M NaOH was added. The material was placed in a freezer (-15°C) to freeze and thaw. Three cycles were done within three consecutive days. At the end of the treatment, the liquor was removed and the material was washed with an ample amount of deionized water (11 liters in total) by centrifugation until the pH of the washing water was at around 10. The material was dried at 50~60°C and homogenized with a ball mill for 5min. The sample was named **TBFZ3**.

2.1.3 Sludge material preparation (SLG)

The sludge collected from a discharge port of a drinking water treatment plant (Sudbury, Ontario, Canada) has a water content of 68 to 90%. Centrifugation was

performed to collect the testing material at 4℃ under a centrifugal force of 12.227G, i.e. 7000 rpm for 30min (Beckman Coulter TM, Avanti TM J-20, XPI, rotor JLA-8.1000, Serial NO. 05U 1435). The supernatant was removed and the remaining sludge was dried at 50~60 ^{o}C. The dry material (SLG) was homogenized with a ball mill for 5min.

2.1.4 Mixture of fly-ash and sludge

Various preparations were used to obtain mixed materials containing both fly ash and sludge as adsorbents. Mixed materials were simply done with mechanic mixing of SLG and Thunder Bay fly-ash with different mass ratios: 4SL:1TB and 1SL:4TB.

The major chemical compositions of the original fly-ash (TB) and the sludge (SLG) samples were measured by ICP–AES following a sodium peroxide fusion, except for Na where a HF digestion and FAAS was employed. The results are presented in **Table 6**. The concentrations of trace elements in TB, TBFZ3 and SLG were measured by a total digestion with HG and graphite furnace atomic absorption spectrometry. The composition percentage of samples was expressed in percentage.

2.2 Analytical Methods and Instrumentation

A PSA 10.055 Millennium Excalibur hydride generation atomic fluorescence spectrometer manufactured by PS Analytical, equipped with a continuous flow hydride generation system and a boosted discharge hollow cathode arsenic or selenium lamp as the radiation source of atomic fluorescence detector, were used in determination of As and Se[109].

The concentrations of Cr(VI), Mo(VI),Cu(II)and Ni(II) were measured by either flame or graphite furnace atomic absorption spectrometry (FAAS or GAAS, Perkin-Elmer AAnalyst 400 or AAnalyst 600) depending on concentrations in solution. Anions present in solutions and TPW were analyzed on a Dionex DC500 ion chromatograph equipped with an ionic conductivity detector.

Images of particles were obtained by scanning electron microscopy (SEM) with a JEOL 6400 equipped with an energy dispersive x-Ray probe Oxford X-max. The identification of crystalline phases in used materials was done using X-Ray powder diffraction on a Philips PW 1820. The anode material was a CO target, and the conditions employed were 40KV and 20mA. Samples were scanned from 10^o to 70^o, 2θ in increment of 0.05^o and at speed of 5seconds.Various crystalline phases in the adsorbents were identified.

A Micrometrics ASAP 2010 (Folio Instruments Inc) was used to determine surface area, adsorption/desorption pore diameters and pore volumes of adsorbents. The sample was dried in the oven for 48 hours at 50^oC to 60^oC, and then 0.1000g of sample was precisely delivered into a sample tube. The Brunauer-Emmett-Teller (BET) analysis was used to evaluate specific surface area based on N_2 multilayer adsorption measured on the testing material as a function of relative pressure using a fully automated analyzer. The technique encompasses external area and pore area evaluations to determine the total specific surface area in m^2/g yielding important information in studying the effects of surface porosity and particle size. The Barrett-Joyner-Halenda (BJH) analysis was used to determine pore area and specific pore volume also using adsorption and desorption techniques. This technique allows obtaining pore size distribution independent of external area due to particle size of the sample. It applies only to the mesopore and small macropore size range.

A particle size analyzer Microtrac S 3000 was used to characterize the particle size distribution.

2.3 Experimental Design

Several sets of experiments were designed in the investigation of the adsorption properties of selected elements on the various materials (modified and non-modified fly ash, and original sludge).

The effect of pH, kinetics time and adsorption isotherms (initial concentration) of the metal(loid) ions on different adsorbing materials were studied.

2.3.1 Determination of the cation-exchange-capacity (CEC) of adsorbing materials with the Kjeldahl method

The Kjeldahl method was used to measure the cation exchange capacity (CEC) of each adsorbent (TB, TBFZ3 and SLG). A portion of 3.00 g each sample was weighted and added to 30mL of 1.0M $NH_4(CH_3COO)$ or NH_4Ac. Samples were shaken horizontally for 17 hours at room temperature (22~25^oC), and then centrifuged for 20min at 2500rpm. The supernatant was rejected. The remaining solid was washed with 8.0mLof 99% (v/v) 2-propanol and this washing procedure was repeated 4-5times (shaking for 10min and centrifuging at 3700rpm) for 20min. The sample was oven dried at 50^oC for 24 hours and then was ready for the Kjeldahl distillation. The distillation apparatus is composed of three parts: a receiver glass flask (250mL), a long necked reactor glass flask (250mL) and cold water condenser connecting the two flasks.A20.00mL aliquot of previously standardized 0.10M HCl was pipetted into the receiver that was tightly connected to the condenser. In the Kjeldahl reactor (0.1 gram of sample was precisely weighed and introduced, followed by 0.5g of Zn metal granular as boiling stone; 20.0mL of 1.0M NaOH was swiftly added into the reactor and the connections were well tightened. The Kjeldahl flask was heated with a heating mantle. The sample in the reactor was boiled for 1 hour. At the end of the distillation, joints were disconnected and the condenser bar rinsed with a little volume of water which was collected in the receiver.

2.3.2 pH evolution measurement

The pH evolution study in different adsorbents with time was systematically performed under two different conditions: (1) immersing the adsorbent in deionized water alone; (2) immersing it in a solution containing a mixture of ions at 50.0μg/mL(50ppm) each. In the study, a 0.500g of adsorbent was transferred into a 50.00mL of deionized water or a 50.00mL mixed ion solution in a HDPE centrifuge tube. The pH values were periodically taken at the top supernatant solution after a centrifugation at 2500rpm for 10min; between each measurement, the sample was subjected to a horizontal shaking at 120 rpm (Gyratory Water Bath Shaker Model G76,

New Brunswick Scientific). The pH meter was calibrated each hour with standard pH buffers of 4.01 and 10.4. During the studies, pH was simply monitored, without any adjustment.

2.3.3 pH effect on the adsorption of different elements

It is very important to study the effect of pH on the adsorption of the studied elements so that it could be controlled. Unlike metal ions with positive charge, the studied anions are not likely involved in precipitation reactions as pH increases. Adsorption tests were performed at various pH to determine the optimum value.

2.3.4 Adsorption kinetic study

For adsorption kinetics, tests were performed in deionized water (DW)in the presence of 0.500g of adsorbent. In the test with DW, a mixed ion solution of 50.0 mg/Land 1.00 mg/L , and 0.500g of adsorbent each was used throughout all the studies.

In the studies, an aliquot of standard stock solution of each element was precisely pipetted into an approximate 40.0 mL of DW (or TPW) water. The pH was adjusted with 0.2M NaOH or 0.2M HCl at 50.00mL, and then placed 0.500g of adsorbent into the solution.

2.3.5 Studies for maximum adsorption capacity of adsorbents in deionized water

These studies were done with a presence of a single element in the system. In this study, a series of 50.0mL solutions of different concentrations of a given element were prepared. A portion of 0.500g of an adsorbent was introduced into the solution. The sample was shaken for 4 hours horizontally (120rpm) until adsorption equilibrium was reached. The sample was centrifuged at 2500rpm for 20 min. The supernatant was carefully collected, acidified with 2% (v/v) HNO_3 and stored in a refrigerator for future analyses. The pH of the solution was adjusted to the value where an optimal condition was demonstrated for a given element and a given material, based on pH effect studies. The pH value was kept as close as possible in one series of test for a given element.

The maximum adsorption capacity of a given adsorbent was obtained experimentally by noting the corresponding q_e value on a plateau of a plot of q_e vs. C_e, which indicates adsorption saturation had been reached.

2.3.6 Studies of adsorption properties of As(V), Se(IV),Cr(VI) and Mo(VI) in a tailing pond water (TPW)

The Vale tailing pond occupies a surface area of 27km^2 and with storage of ~637 million tons of tailings immersed under water. Before being returned to the natural environment, the surface waters are sent to a waste water treatment plant through a creek of 3-4 km long. For my study, 25L of the untreated mining wastewater was collected on Oct 26, 2015. For the chemical composition test, two aliquots of subsamples were taken; one was filtered through 0.2μm Millipore membrane and another was kept without filtration. These subsamples were acidified with HNO_3 to obtain 2% acidity. For metal concentrations in the water, flame or graphite furnace atomic absorption spectrometry was used and for anions, ionic chromatography was employed.

This tailing water was used to perform adsorption properties of the studied materials. The adsorption kinetics was examined in pristine TPW, in a TPW spiked with either 1.0or 50μg/mL of a mixed elemental solution of each. Similarly, the adsorption capacity of the materials to a given element was also studied in presence of a single element. The other details of operational processes are the same as in 2.3.4 and 2.3.5. The experiments were performed immediately after the water was collected from the creek and completed within 1 week. The water sample was stored at 7^{o}C in a refrigerator. It was noticed that with time, some iron oxyhydroxides were formed during storage.

2.3.7 Test on trace element leaching from the testing adsorbing materials

For this test, 0.500g of adsorbent was precisely weighed and placed into a 50 mL of high density polypropylene centrifuge tube. 50.00mL of deionized water was introduced. The sample was undergone a continuous horizontal shaking at 120rpm for 10 consequent days (T=22±2^{o}C). An aliquot of 1.00mL was pipetted at any given time and centrifuged. The supernatant was carefully taken and acidified with HNO_3 to 2%. The concentrations

of elements in the leaching solution were determined by GFAAS or HG-AFS (for As and Se). For Mo analysis, N_2O was used as an oxidant in flame atomic absorption spectrometry (FAAS) to improve its sensitivity. Due to the low sensitivity of Mo in FAAS, most Mo analysis was done with graphite atomic absorption spectrometry (GAAS), except when 50mg/L spiked Mo was to be measured.

For total As measurements for both DW and TPW analysis, 3.6% (w/v) KI in 3.0M HCl was used to pre-reduce As(V) to As(III) before measurement. The total Se in TPW was measured in a sample with a pre-reduction in 3.0M HCl at 110^{o}C for 15min in a microwave oven [110].

Chapter 3 Results and Discussion

Apart from toxic metal cations in wastewater, some other inorganic anions exist in waters and could be dangerous for human health. Among those, four inorganic anions have been the focus of this study, arsenate (AsO_4^{3-}), selenite (SeO_3^{2-}), chromate (CrO_4^{2-}) and molybdate (MoO_4^{2-}). This thesis is focussed on the modification of fly ash from Thunder Bay Power Generation Plant and the application of drinking water sludge to evaluate their potential for the removal of oxyanions (AsO_4^{3-}, SeO_3^{2-}, CrO_4^{2-}, MoO_4^{2-}, occasionally that of Ni^{2+} and Cu^{2+}) from mine tailings and effluents.

3.1 Chemical and physical characterization of adsorbents

The pristine adsorbents of Thunder Bay fly-ash (**TB**) and the sludge of drinking water plant (**SLG**) were chemically and physically characterized. The major chemical compositions of the original fly-ash and the sludge samples and the concentrations of trace elements in TB, TBFZ3 and SLG are presented in **Tables 6** and **7**.

Elemental analysis of the materials confirmed that aluminum was the highest chemical element in TB and SLG. In the fly-ash sample **TB**, the second highest in composition was silicon, followed by calcium and magnesium. The presence of relatively high concentration of CaO, MgO and Na_2O reveals the alkaline nature of the fly-ash sample. It is important to note that there is an important fraction of iron in both fly-ash and sludge samples that could play a crucial role in the metal ion adsorption process. In the sludge sample, the aluminum is of predominant element, as the drinking water treatment plant uses $Al_2(SO_4)_3 \cdot 14H_2O$ (aluminum sulfate) as a coagulant to remove contaminants from water.

In the two materials, the concentrations of the elements of interest［As(V), Cr(VI), Mo(VI), Se (IV), Cu(II) and Ni(II)］were very low (**Table 6**). It is noticed that the trace elements present only a very low concentrations in these materials. To estimate the potential release of these elements in environmental, a leaching test was conducted. The

leaching test showed that there is no measurable amount of trace elements during the 10 days of test. This means that the trace elements in the materials are in refractory form and will produce restricted negative effect. However Se is exceptional as Se concentration in the leaching solution had a quick increase to 17μg/L in the first 4hours, then slowly increased to 23μg/L after 72hours and stabilized there. It is assumed that the Se in TB sample was presented in a water soluble form of SeO_2 or SeO_3^{2-}. This hypothesis is confirmed by the fact that Se in TBFZ3 was much lower than in TB, as the former was subjected to intensive washing after the NaOH modification with freeze /thaw cycles. If the fly ash was treated in alkaline water, the Se can be easily removed.

Table 6 Major Chemical composition of the original fly-ash and the sludge samples measured by ICP-AES.

Sample ID	**Al** (%)	**Al_2O_3** (%)	**As** (%)	**B** (%)	**Ba** (%)	**Be** (%)	**Bi** (%)	**Ca** (%)	**CaO** (%)	**Cd** (%)	**Co** (%)	**Cr** (%)	**Cr_2O_3** (%)
TB	9.61	18.16	0.002	0.061	1.18	<0.0000	<0.0020	11.1	15.53	0.0001	0.005	0.011	0.0161
SLG	20	37.79	<0.0020	<0.0025	0.015	<0.0000	<0.0020	0.3	0.4198	0.0001	0.005	0.006	0.0088

Sample ID	**Cu** (%)	**Fe** (%)	**K** (%)	**Li** (%)	**Mg** (%)	**MgO** (%)	**Mn** (%)	**Mo** (%)	**Ni** (%)	**P** (%)	**Pb** (%)	**S** (%)	**Sb** (%)
TB	0.044	3.621	0.611	0.005	2.22	3.681	0.036	0.002	0.093	0.109	0.004	2.6	0.012
SLG	0.052	0.38	0.049	<0.0002	0.025	0.0415	0.009	0.001	0.109	0.97	<0.0012	0.9	0.017

Sample ID	**Se** (%)	**Si** (%)	**SiO_2** (%)	**Sn** (%)	**Te** (%)	**Ti** (%)	**TiO_2** (%)	**V** (%)	**Zn** (%)	**Vale sum** (%)	**Na FAAS*** (%)	**Na_2O** (%)	**final sum** (%)
TB	0.015	16.58	35.46	0.012	<0.0015	0.691	1.152	0.0151	0.075	89.23	5.43	7.319	96.55
SLG	SLG	0.02	1.857	3.972	0.019	<0.0015	0.008	0.0133	0.0019	0.004	45.14	<DL	45.14

Table 7 Major chemical compositions of pristine materials

Chemical compositions (%)	**Drinking water sludge (SLG)**	**Thunder Bay Fly-ash (TB)**
Al_2O_3	37.79	18.16
SiO_2	1.86	16.58
CaO	0.42	15.53
Fe_2O_3	4.05	4.32
MgO	0.04	3.68
Na_2O	< D.L.	7.32
S	0.9	2.6

Table 8 The trace element concenrtations in twotesting materials, measured by GFAAS.

TM	Co mg/kg	Cd mg/kg	Mo mg/kg	Cr mg/kg	Pb mg/kg	Ni mg/kg	Zn mg/kg	Cu mg/kg	Sb mg/kg	As mg/kg
SLG	N.D.	0.3	N.D.	11.6	3.4	54.2	38.7	40.3	3.2	5.7
TB	N.D.	1.0	12.6	43.6	34.3	58.0	90.1	138.3	9.4	15.7
TBFZ3	N.D.	1.4	2.8	34.7	40.3	61.0	80.3	143.4	1.5	6.7

3.2 The surface characteristics of adsorbents materials

3.2.1 Morphological observation

The pristine fly-ash samples from Thunder Bay are composed of characteristic smooth and ball-like particles (**Figure 4**). After TB samples had been treated with the freezing/thawing cycles significantly increased surface areas and material pore volumes could be observed(**Figure 5**).

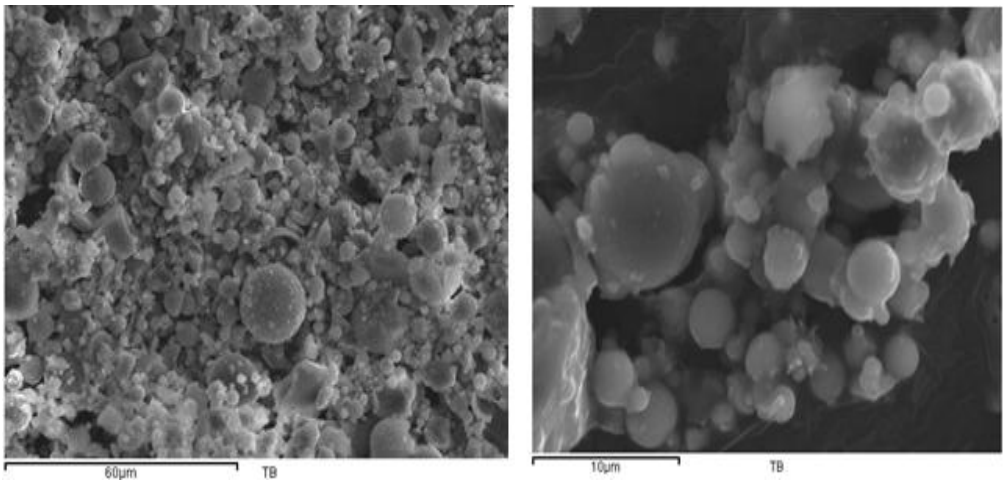

Figure 4 SEM photos of non-modified fly ash from Thunder Bay Scale of 60µm (left) and 10µm (right)

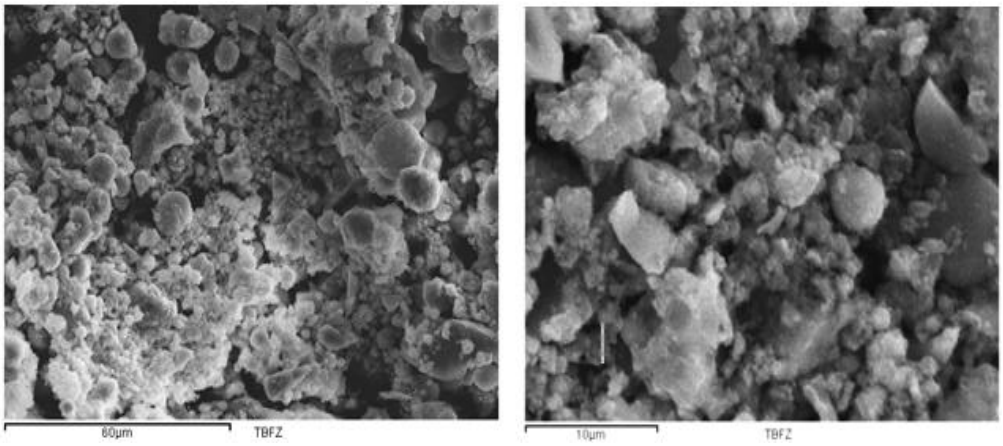

Figure 5 SEM photos of Thunder Bay fly-ash treated with 2.0M NaOH, and the freezing/thawing 3 cycles in 3 days, scale of 60µm (left)and 10µm (right)

The pristine drinking water sludge is amorphous and aggregated in appearance (**Figure6**). This material was principally mainly used in the adsorption studies of oxyanions.

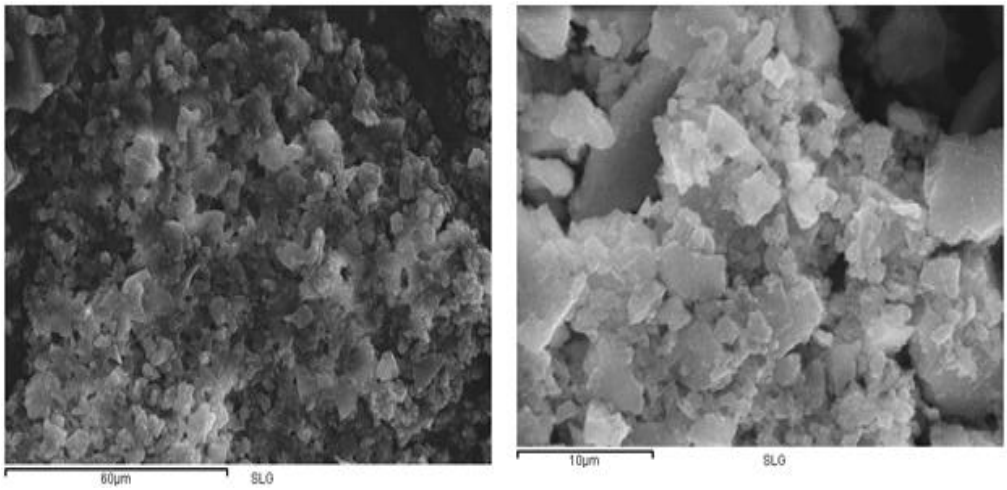

Figure 6 SEM photos of non-modified drinking water sludge (SLG) Scale of 60µm (left) and 10µm (right)

3.2.2 The particle size and surface properties

Among the two original materials, SLG possesses the higher surface area and porosity (BJH accumulative pore volume), followed by TB. In term of particle size, TB is the smaller than SLG.

Table 9 Morphological characteristics of the pristine adsorbent samples

Parameter	**unit**	**TB**	**SLG**	**TBFZ3**
BET surface area	m^2/g	1.24	171.28	13.24
BJH accumulative pore volume	cm^3/g	0.0036	0.3190	0.0345
Mean volume diameter	µm	12.6	54.22	N/A
mean number diameter	µm	0.769	1.606	N/A
mean area diameter	µm	3.3	10.44	N/A

Table 9 shows a comparison of the surface properties of a pristine Thunder Bay fly-ash sample TB with a treated sample TBFZ3. In general, the surface area of the modified material was remarkably increased for Thunder Bay fly-ash. The freezing/thawing- 2.0M

NaOH treatment increased the particle surface area and adsorption/desorption pore volume. For TB fly-ash, the surface area increased from 1.24 m^2/g to 13.24(ID # A2), representing more than a 10-fold increase, which is of the same order of magnitude of the adsorption/desorption pore volume. Data in **Table 9** indicate that TB fly-ash seems less rigid and easier to be broken down after the treatment as its surface area has been increased many times.

When particles became smaller, more pores were created and the diameter of pores decreased. It can be seen from **Table 9** that, apart from the BET surface area of adsorbents increasing from 1.24 m^2/g (TB) to 13.24 m^2/g (TBFZ3) that of the sludge was estimated at 171.28 m^2/g (SLG).The pore volume for fly ash increased from0.0037 cm^3/g (TB) to 0.0345 cm^3/g (TBFZ3) and was measured at 0.3190 cm^3/g for SLG with a decreasing average particle size of TB, TBFZ3 and SLG. Higher specific surface areas and pore volumes and more pores were beneficial to the adsorption process as demonstrated further in the section and confirmed the validity of using BET and BJH calculations.

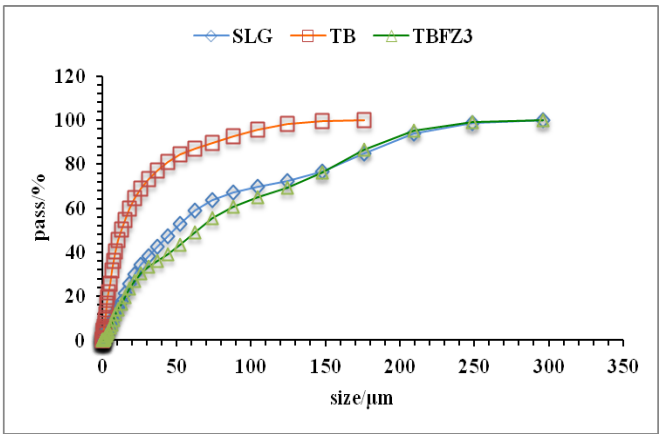

Figure 7 Grain size distribution of TB, TBFZ3 and SLG

The results of particle size analysis show **(Figure 7)** a size 296μm for SLG corresponding to 100% pass, which was the same value for TBFZ3. However for TB, the particle size corresponding to 100% pass was only 176μm confirming thatTBFZ3 and

SLG have larger particle sizes than TB, probably due to the aggregation of these two types of materials.

3.2.3 Mineralogical studies of the adsorbents

A comparison of XRD results of unmodified TB to the frozen samples reveals differences in the mineralogy of the two samples. It shows that the peak of Al_2O_3 observed in the original fly ash, does no longer appear in the modified sample TBFZ3, which is probably due to the activating agent (2.0M NaOH) and the integration of Al_2O_3 in other mineral structures. In fact, calcium carbonate and silicon oxide were very prominent in both samples. In TBFZ3, calcium carbonate, silicon oxide and sodium aluminum silicate sulfate were able to withstand the freezing/thawing treatment with NaOH, thus peaks of the three minerals were identified just as in the original TB (**Table 10** and **Figure 8**). The sludge is composed mainly of Al_2O_3 and iron oxides (Fe_2O_3) in non-crystalline forms.

Table 10 Comparison of crystallinity of TB and TBFZ3 by XRD

TB			**TBFZ3**		
Color code	**Mineral Name**	**Chemical Formula**	**Color code**	**Mineral Name**	**Chemical Formula**
Blue	Sodium Aluminum Silicate Sulfate	$Na_8(SO_4)(Al_6Si_6O_{24})$	Blue	Calcium Carbonate	$CaCO_3$
Green	Calcium Carbonate	$CaCO_3$	Green	Sodium Aluminum Silicate Sulfate Hydrate	$Na_8(SO_4)(Al_6Si_6O_{24})(H_2O)_{0.96}$
Grey	Silicon Oxide	SiO_2	Grey	Silicon Oxide	SiO_2
Pink	Aluminum Oxide	Al_2O_3	Pink	Sodium Aluminum Silicate Sulfate	$Na_8(SO_4)Al_6Si_6O_{24}$
Light blue	Bismuth Vanadium Oxide	$BiVO_4$			

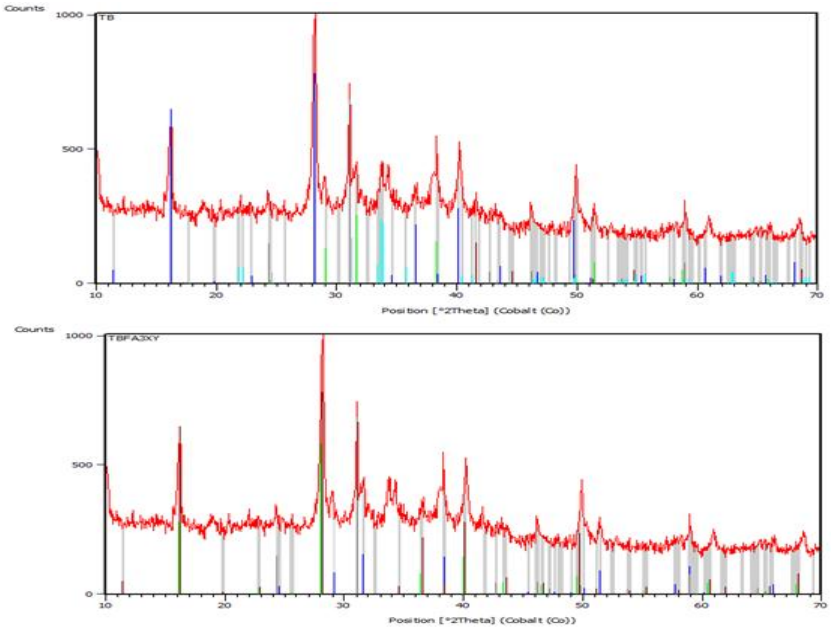

Figure 8 X-Ray diffraction pattern of two samples, TB (top) TBFZ3 (bottom)

Thunder Bay fly-ash was soaked in 2.0M NaOH solution and treated under a series of freezing/thawing cycles to evaluate the possible breaking down of the fly-ash to still smaller particles by expansion of frozen water. This process would be energy saving under Canadian winter weather conditions. Also, TBFZ3 showed similar adsorption properties to tested metal ions, although it demonstrated slightly higher adsorption efficiency. Because of the advantages of low energy consumption, simple operational process and large sample preparation, the modification protocols at low temperature were employed and the modified fly-ash TBFZ3 was used in later experiments.

3.2.4 The surface cation-exchange- capacity (CEC) of the adsorbents

The surface cation-exchange capacity of an adsorbent is an important parameter in estimation of an adsorbent, because the adsorption efficiency of the adsorbent strongly depends on CEC. When CEC increases, there will be more exchangeable cations retained by the adsorbents [111].

The general principle of the Kjeldahl method is as follows:

(1) replace the cations on the surface of the sample with 1.0M NH_4Ac

$$\text{Solid phase} -M + nNH_4^+ \rightarrow n \text{ solid phase} -NH_4 + M^{+n}$$

(2) use Kjeldahl distillation to release NH_4^+ from solid phase in form of NH_3 in Kjeldahl flask

$$\text{Solidphase} -NH_4^+ + NaOH \rightarrow \text{solidphase} + NH_3\uparrow + Na^+ + H_2O$$

(3) the released base $NH_{3(g}$ from the reactor will be quickly dissolved in aqueous phase first, then it will react with added HCl acid (in excess) in the receiver

$$NH_{3\,(g)} \rightarrow NH_{3(aq)}$$

$$NH_3(aq) + HCl \rightarrow NH_4^+ + Cl^-$$

(4) titrate excess acid (HCl) with standardized NaOH solution using the Bromocresol indicator.

Calculation of CEC of measured sample (meq/g):

$$CEC = [C_{HCl} * V_{HCl} - C_{NaOH} * V_{NaOH\ titrated}]/\text{sample weight}]*100g$$

CEC value is expressed as millimole electrical charge equivalent per gram of sample.

The Kjeldahl distillation technique has an advantage of minimizing the possible interference compared to other technique such as determination of total concentration of all cations, although it is time consuming and skill demanding.

The average CEC of SLG, TB and TBFZ3 were 55.03, 3.32 and 15.45 meq (milli-equivalent mole)/g, respectively. Comparing among the three adsorbents, SLG showed a greatest cation exchange capacity, followed by TBFZ3 and TB. It is noticed that the CEC of TBFZ3 was around 5 times higher than that of non-modified TB, therefore it is expected that the adsorption capacity of TBFZ3 be better than non-modified TB.

3.2.5 Trace element leaching test of adsorbing materials

The utilization of the three adsorbents materials (fly ash, sludge and modified TBFZ3) in water could involve a potential leaching of some elements into water and thus cause a problem of secondary environmental pollution. It has been found that the surface layer of fly ash particles of probably only microns in thickness could contain a significant amount of readily leachable material which is deposited during cooling after combustion [112].

The results showed that all environmentally concerned trace elements are in non-detectable levels (< 3μg/L), except Se in TB sample. This is because in the high temperature furnace, the large majority of these elements are emitted in gaseous forms of oxides and released to the air, any trace amounts remaining in fly-ash would be in refractory forms and would not be easily water, therefore does not present as an environmental threat.

As to Se, it is assumed that the quick increase of Se in leachate of TB system and stabilized concentration thereafter indicates the presence of dissoluble SeO_2 and SeO_3^- on the surface of fly ash. This form of Se was washed away from the material TBFZ3 after it reacted with NaOH. The remaining Se should be also in refractory and non-water soluble form.

Trace metal concentrations in the leachate depend on ratio between adsorbents weight and solution, pH, concentration of the elements, temperature, pressure and time. It is recommended to conduct a similar test over a longer period and with a realistic solid/liquid ratio.

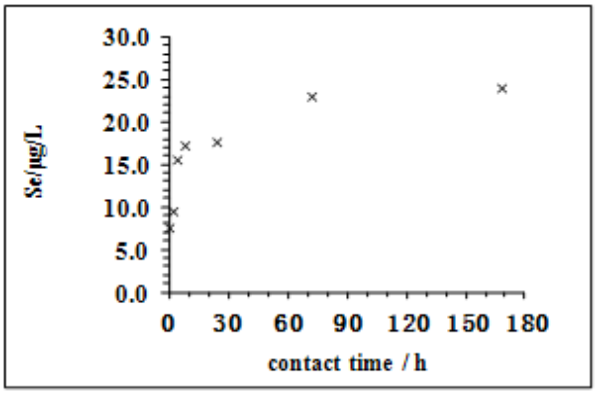

Figure 9 The release of selenium from TB in DW with time. Leaching test involved 0.500g of given adsorbent immersed in 50.0mL of deionized water under constant shaking (pH 7.20±0.08)

3.3 Adsorption properties of materials

The potential of fly-ash and drinking water sludge as an adsorbent for metal removal was investigated indifferent aqueous systems spiked with several selected metal/metalloid ions. Four oxyanions of high environmental concerns were selected in the studies: arsenate (As^{V}, AsO_4^{3-}), selenite (Se^{IV}, SeO_3^{2-}), chromate (Cr^{VI}, CrO_4^{2-}) and molybdate (Mo^{VI}, MoO_4^{2-}).

In our earlier studies, we have attempted to modify a mixture of TB and SLG by cooking it in 2.0M NaOH liquor at high temperature (150^{o}C for 4hours). It failed because the dissolution of SLG under such conditions, due to the amphiprotic properties of iron oxide and aluminium oxide. The product such treatment showed a much reduced adsorption properties towards studied oxyanions compared to SLG and fly ash alone. On another hand, these data showed that the important role of $Al(OH)_3$ and $Fe(OH)_3$ in adsorption processes.

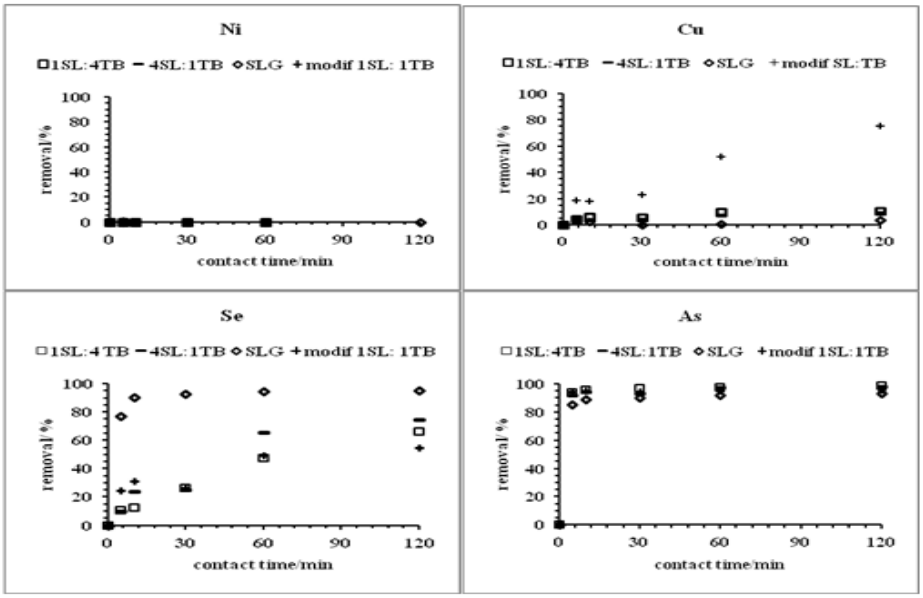

Figure 10 Kinetics test in 50.00mL of 50mg/L of the mixed solution［Se(IV), As(V), Ni^{2+} and Cu^{2+}］without adsorbent at T=22±2°C , t= 2 hours; constant shaking at 120 rpm.

From the kinetics test in 50.00mL of 50mg/L of the mixed solution [Se(IV), As(V), Ni^{2+} and Cu^{2+}], the pH was not controlled, a pH range of 1.44 to 3.30 was applied in this studies. Based on the observation of **Figure 10,** sludge was the good adsorbent for Se(IV) and As(V) when the solution was acidic. However, at lower level of pH, the adsorption of Ni(II) and Cu(II) did not take place. It was necessary to control pH properly to compare the removal percentage among these three adsorbents.

In our further studies, the mixed adsorbents systems were only prepared with a mechanical homogenization. The studies were first carried out in deionized water. To have a better evaluation of the adsorption capacities of the tested materials, TPW was used to approach a real waste mining water situation. The water from the tailing pond was collected just before it entered into the water treatment plant.

In the bottom of the creek, there was a heavy deposition of iron oxide. The collected water was very acidic with a pH of 3.36. The water looked quick clear and with very little visible particulate matter (**Figure 11)**.

Figure 11 Vale Tailing Pond Water collected in a stream out flowing from the pond and going to the water treatment plant.

3.3.1 Chemical characterization of Vale Tailing Pond Water

The chemical composition of the collected TPW is presented in **Table 11**. To check the potential influence from particulates on the concentrations of tested elements, the TPW sample was subdivided into 2 aliquots: one was filtered through a 0.2μm membrane and the second one was not filtered; 50.0mL of each aliquot was taken and acidified immediately to 2% (v/v) HNO_3. For anions analyses, the sample was filtered but not acidified. It was found that the concentrations of cations in the 0.2μm filtered water showed little difference from that of non-filtered water sample confirmed that the content of particle matter is indeed negligible. **Table 11**, the combined concentrations of filtered and non-filtered samples were used in further calculations and discussions.

The collected water contains high concentrations of dissolved sodium, magnesium and calcium and moderate concentrations of potassium and iron. The concentrations of environmentally concerned cobalt and copper were high in this water, 0.36 and 4.26mg/L, respectively; Ni was particularly high with a concentration of 16.0 mg/L or 0.273mmole/L. The concentrations of other trace elements were very low. In terms of anion concentrations, $SO_4^{2-}$was the highest and reached 664.2mg/L (20.7mmol/L), followed by Cl^- at 127.6ppm (3.6mmol/L). This also explains a low pH of 3.36 (SD 0.006, RSD 0.17%, n=3) of this water. Comparing to Cl^- and SO_4^{2-}, the concentrations of other anions are much lower and should not present a serious influence on adsorption processes.

Trace elements concentrations of testing materials were determined by graphite furnace atomic adsorption spectrometry and Hydride generation atomic fluorescence spectrometry.

Table 11 The chemical compositions and concentrations of elements in Vale Tailing Pond Water

Classification	Sample ID	unit/statistics	**Na**	**K**	**Ca**	**Mg**	**Fe**	**Mn**			
Major cations (FAAS)	0.2**μm Filt.**	mg/L	119.59	33.34	375.90	82.10	68.10	1.61			
		mmole/L	5.20	0.85	9.38	3.38	1.22	0.03			
	non- **Filt.**	mg/L	116.70	32.65	369.00	83.20	65.20	1.54			
		mmole/L	5.08	0.84	9.20	3.42	1.17	0.03			
	combined	mg/L	118.14	33.00	372.45	82.65	66.65	1.58			
		mmole/L	5.14	0.84	9.29	3.40	1.19	0.03			
Studied metals (GAAS, HG-AFS)	**0.2μm Filt.**		**Tot As**	**Cd**	**Co**	**Tot Cr**	**Cu**	**Mo**	**Ni**	**Pb**	**Tot Se**
		Avg/μg/L	0.8	5.2	349.0	7.9	4257.2	0.7	16116.9	6.3	
		SD or △ /2	0.054	0.0853	1.5	0.13	134.9		35.8	2.4	
		RSD%	6.81	1.65	0.4	1.69	3.2		0.2	37.7	
		n	3	3	2	3	2	1	2	4	
		Avg/μmol/L	0.011	0.046	5.922	0.152	66.994	0.007	247.611	0.030	
	non-Filt.	Avg/μg/L	1.48	5.20	347.9	8.71	4712.1	0.68	15931.3	6.50	4.89
		SD or △ /2	0.213	0.103	1.3	0.27	171.8		35.8	1.40	0.10
		RSD%	14.33	1.98	0.4	3.1	3.6		0.2	21.5	2.0
		n	3	3	3	3	2	1	2	4	3.00
		Avg/μmol/L	0.02	0.05	5.90	0.17	74.15	0.01	271.45	0.03	0.02
	combined	μg/L	1.14	5.19	348.45	8.32	4484.65	0.67	16024.11	6.40	1.38
		μmol/L	0.015	0.046	5.913	0.160	70.573	0.007	273.030	0.031	0.017
Anions (IC)	**0.2μm Filt.**		**F^-**	**Cl^-**	**NO_2^-**	**PO_4^{3-}**	**NO_3^-**	**SO_4^{2-}**			
		Avg/mg/L	0.16	127.63	—	0.31	0.70	664.17			
		SD//mg/L(n=3)	—	19.1	—	—	—	97.0			
		Avg/mmol/L	0.01	3.6	—	0	0.05	20.72			

Note: the concentration of anions expressed in mg/L of the mass of the given element, not the formula weight of its oxyanion.

3.4 pH evolutions in different adsorption systems

The adsorption of an inorganic anion is highly dependent on surface charge of an adsorbent which in turn is greatly affected by pH of the adsorbing system. Typically its adsorption reaches to a maximum close to the pKa for the protonated form of the adsorbing anion before decreasing markedly with further rises in pH[113,114]. For instance, for adsorbent with S-OH rich surfaces, its surface charge can varies as the pH of the system changes according to equilibria (3.4.1) and (3.4.2). When pH decreases ($[H^+]$ is high), the reaction (1) shift leftward, the surface charge become positive; when pH increases ($[OH^-]$ increases), OH^- will neutralize H^+ and induces the equilibrium of reaction 2 rightward, making the surface negatively charge, which will be unfavourable for anion adsorption due to greater electrostatic repulsion.

$$\equiv S\text{-}OH_2^+ < == > \equiv S\text{-}OH + H^+ \qquad (3.4.1)$$

$$\equiv S\text{-}OH < == > \equiv S\text{-}O^- + H^+ \qquad (3.4.2)$$

where ≡S-OH represents an adsorbent site (S represent Al, Si, Fe, Ti, etc.).

For this reason, the pH values of the solution were periodically measured and adjusted when necessary to ensure that adsorption had taken place consistently at the desired pH values.

3.4.1 pH evolution of different adsorbents in deionized water and TPW

pH evolution of different adsorbents in deionized water

Adsorption processes are closely associated to surface properties of an adsorbent, such as surface area, surface charge and chemical state of the functional groups, pH of the system, as well as to the chemical properties of adsorbate. The pH of a studied system is directly dependent on the nature of the adsorbent and the system under study. When immersed in deionized water, the pH evolution of the studied adsorbing systems (**Figure12**) was relatively constant in the periods of 2 and 4hours. Among the three adsorbents, SLG had a lowest pH, followed by TB and TBFZ3. When the adsorption

systems were spiked with standard stock solutions of oxyanions, the pH of the system was significantly reduced, due to the acidity of these stock solutions (**Figures 13 & 14**). The pH of SLG system increased from 2.0 to 4.1 after 5hours of contact, whereas in both TB and TBFZ3, the pH rose less rapidly from an initial increase from 3.2 to 4.1 in the first 60 min, and then kept more or less constant.

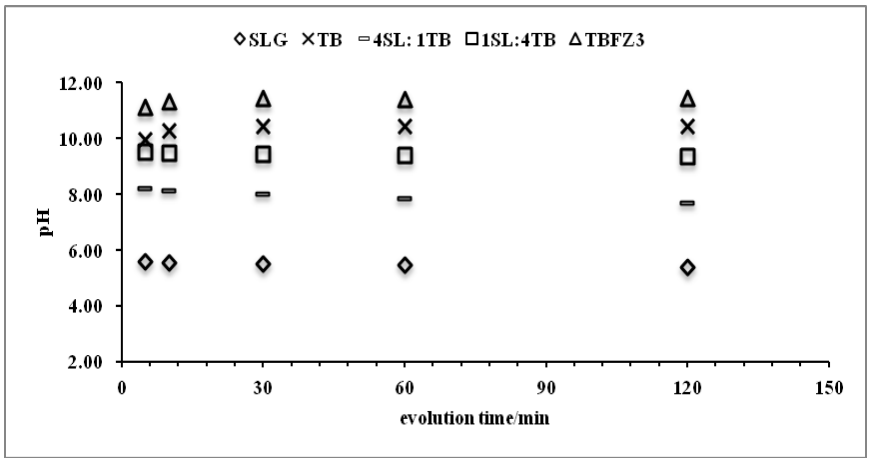

Figure 12 The pH evolution of 0.5000g adsorbents in 50.0 mL of deionized water, T=22±2°C; constant shaking at 120 rpm. (SL = SLG)

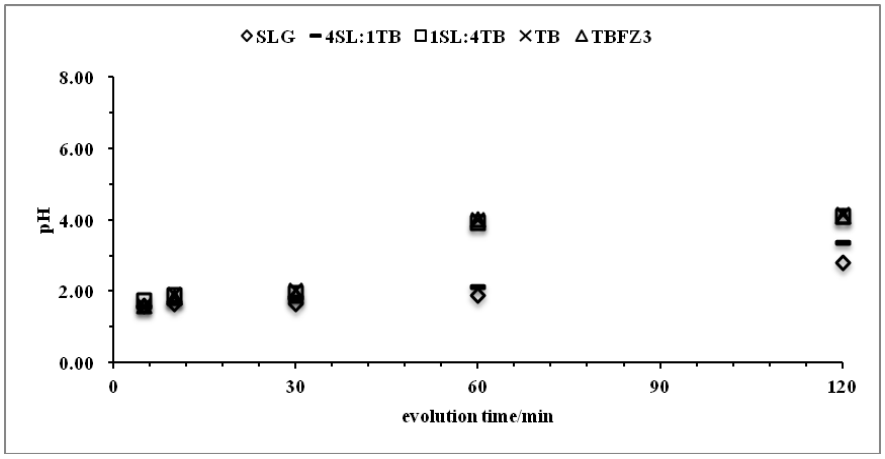

Figure 13 pH evolution of 0.5000g of adsorbent in 50.00mL of mixed solution [Ni^{2+}, Cu^{2+}, Se(IV), As(V), Mo(VI) and Cr(VI)] 50.00mg/L each (T=22±2℃; constant shaking at 120 rpm). (SL = SLG)

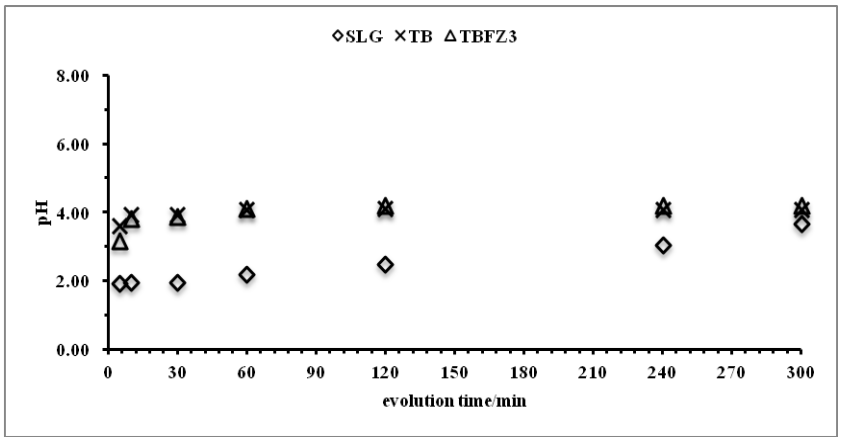

Figure 14 pH evolution of 0.5000g adsorbent in 50.00mL of mixed solution ［Cr(VI), Mo(VI), Se(IV) and As(V)］of 50.00mg/L each (T=22±2℃; constant shaking at 120 rpm).

pH evolution on different adsorbents with TPW

The pH evolution of three types of TB, SLG and TBFZ3 in Vale Tailing Pond Water are given in **Figure 15**. It was found that the SLG has the lowest pH comparing to TB and TBFZ3. When the system was without spiking standard stock solutions of oxyanions, the pH of SLG, TB and TBFZ3 gradually increased from 4.42 to 5.32, 5.48 to 8.7 and 6.73 to 9.07 in 4h. Comparing to those in the systems prepared in deionized water. From these preliminary tests, it was helpful for adjusting the pH by adding 0.2M HCl or 0.2 NaOH in the future studies.

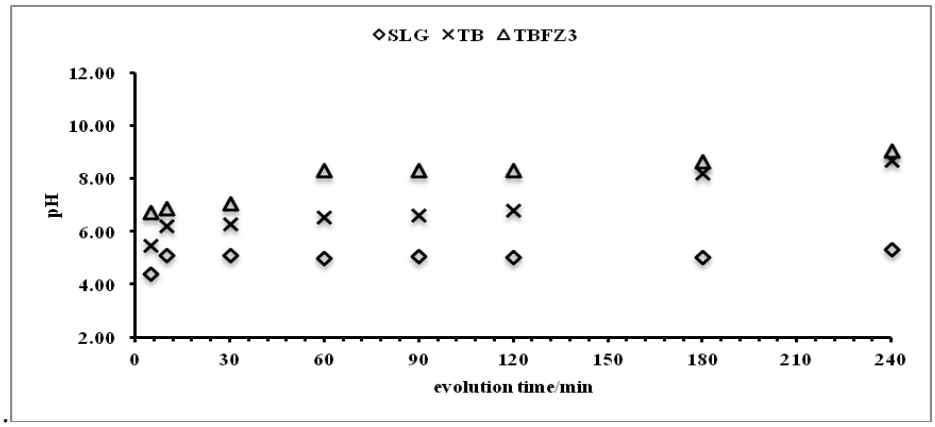

Figure 15 pH evolution of 0.5000 g of adsorbent in 50.00mL of TPW (T=22±2℃; constant shaking at 120 rpm).

3.4.2 pH effect on the element removal in deionized water

The interaction of oxyanions at the water/solid interface of three different adsorbents was investigated in these studies. The effect of pH varies from one adsorbent to another and from one oxyanion to another.

pH effect on adsorption in a cocktail solution of Ni^{2+}, Cu^{2+}, Se(IV) and As(V) prepared in deionized water

It was noticed that the removal curves of Cu and Ni are remarkably different from that of oxyanion Se and As. Although both Cu and Ni removal increased as pH increased, Ni^{2+} removal demands a higher pH than Cu^{2+}. The results also showed that the removal of Cu and Ni has a similar behavior on all three materials, either it was on pure SLG or SLG and TB mixed adsorbent system.

In pH effect study with presence of metallic cation, it is necessary to consider the potential precipitation of these ions in a high pH system ($M^{2+} + 2OH^- \Leftrightarrow M(OH)_2$). The critical pHs ($pH_{critical}$) for a Ni and Cu to form hydroxide precipitate at a given concentration are calculated and given in **Table 12.**

Table 12 The critical pHs for metallic cations form hydroxide precipitate at 50mg/L

Element	μg/L form	The critical pHs for metallic cation form hydroxide precipitate at 50mg/L
Ni	$Cu(OH)_2$	6.26
Cu	$Ni(OH)_2$	8.19

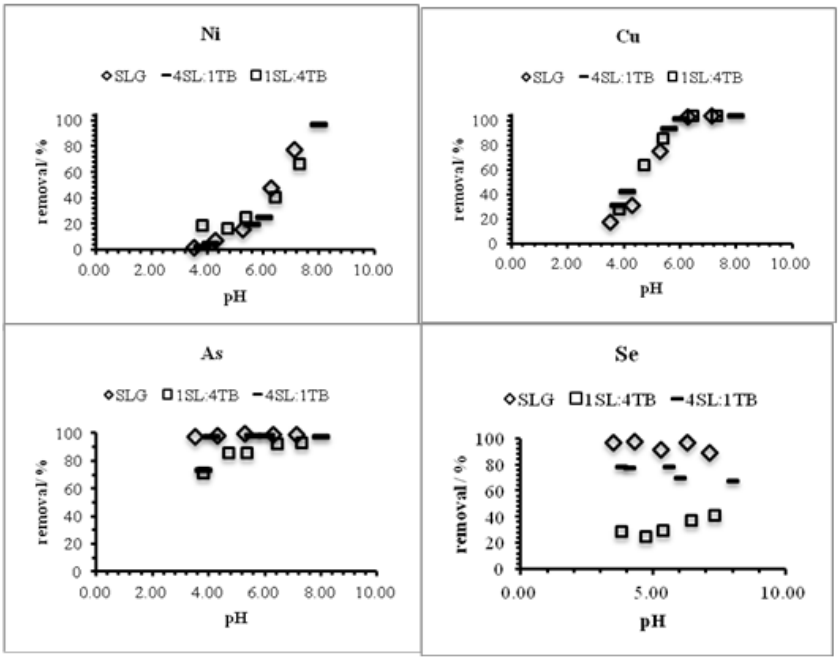

Figure 16 pH effect on elemental removal performed using 0.5000g of adsorbent in 50.00mL mixed solution (Ni^{2+},Cu^{2+}, Se (IV) and As (V)) at 50.0mg/L each, prepared in deionized water (T=22±2℃, t= 2 hours; constant shaking at 120 rpm). (SL = SLG)

The experiments on adsorption efficiency under different pH showed that arsenate, As(V), was the least affected by pH and was the element most effectively removed by all three materials. The best material for As(V) removal was SLG, which adsorbed more than 99% of the element from the system between a pH range of 3.6-7.7. TBFZ3 exhibited a higher efficiency compared to TB, and both types of fly ash showed a reduced As(V) removal effectiveness as pH of the system increased (**Figure 16**).

Selenite, Se(IV) adsorbed well on SLG at a lower pH range (3.7-5.2) with a removal of 95-97% (**Figure 16**). As the pH of system increased further (pH 7.7), the removal dropped to 85%. In TB and TBFZ3 system, pH drastically affected the adsorption of Se(IV), i.e. removal dropped from 85 to 18% as pH increased from 3.8 to 7.9 for TBFZ3, and 71 to 1% as pH went from 4.0 to 7.6 for TB. The possible surface charge transfer can explain this from positive to negative as the concentration of [OH^-] increased in the system.

Precipitation test-significance of reaction

As the concentration of an ion in a solution is increased, precipitation of a new solid phase will not occur until the solubility product of that specific phase has been reached or exceeded. A degree of supersaturation is required because crystal nuclei can only be formed after an energy barrier has been overcome. Metal cations are most likely to precipitate as oxides, hydroxides, carbonates, sulphides, or phosphates. In solutions of natural waters or waste waters where an adsorbent material has been added, the mineral and/or organic surfaces thus present can catalyze the nucleation step of crystallization. The pH and ionic strength of the solution are important factors. Maximum adsorption of different metals occurs at widely different pH values, so that selectivity will be greatly affected by ambient pH. Indeed, specific adsorption of metal cations is strongly pH-dependent. As pH is raised, hydrolysis of hydrated cations proceeds and, in addition, the charge on the variable charge adsorption surfaces becomes increasingly negative (thus favoring adsorption of cations).

Figures 17 almost certainly represented an adsorption/precipitation continuum. That is, as the pH was raised, specific adsorption was promoted, but as adsorption sites become saturated, metal ions cluster onto metal oxide/hydroxide nuclei. Ultimately, the precipitation of $Cu(OH)_2$ and $Ni(OH)_2$ occurred at the surface. The adsorption necessarily reaches 100% adsorption at high pH, as precipitation ultimately removed all the strongly Ni^{2+} and $Cu^{2+}$from solution.

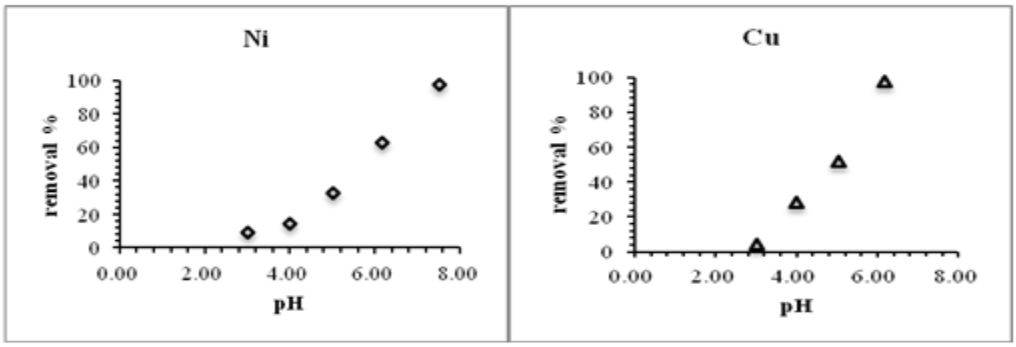

Figure 17 Surface precipitation for Ni^{2+} and Cu^{2+} on amorphous iron hydroxide surfaces as a function of pH.

pH Effect of pH on adsorption in a cocktail solution of Se(IV), As(V), Mo(VI) and Cr(VI) prepared in deionized water

As illustrated in **Figures 16 & 18**, the removal efficiencies of inorganic anions by the different adsorbents were different, and all adsorbents were particularly efficient for As(V). Because the affinity of each anion toward adsorbent was different from one to another, the pH effects on their adsorption appeared also different.

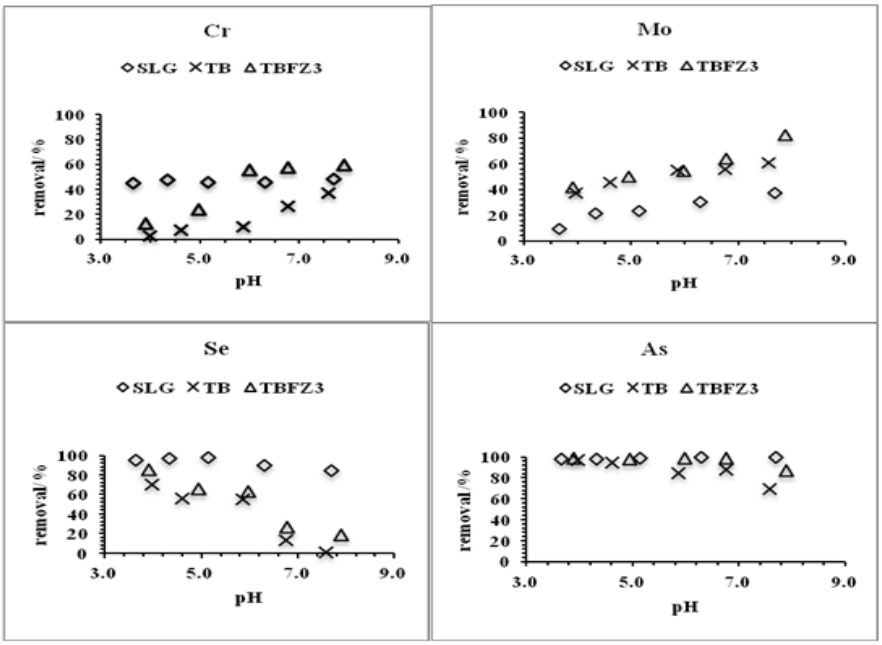

Figure 18 pH influence on elemental removal from different adsorbing systems made up with 0.5000g of adsorbent in 50.00mL mixed solution of 50.00mg/L each (Se(IV), As(V), Mo(VI) and Cr(VI)) (T=22±2℃ , t= 4 hours, constant shaking at 120 rpm).

As it has mentioned earlier, the effect of pH can also be explained in terms of pH_{pzc} (point of zero charge) of the adsorbent. When pH < pH_{pzc}, the positively charged surfaces on the adsorbents would likely prefer the adsorption of the negatively charged As(V) oxyanion, $H_2AsO_4^-$. The greater adsorption of As(V) than other oxyanions was believed to be partly due to the high affinity of Fe oxides to As(V), in which pH_{pzc} for Fe oxide is in the pH range of 6–8. **Figures 12-15** illustrate the effect of solution pH on the uptake of oxyanions from deionized water.

The declining trend in the adsorption of Se(IV) and As(V) with increasing pH showed evidence of similar behavior to that of surface charge density of all three adsorbents (TB, SLG and TBFZ3). However, Mo(VI) and Cr(VI) removal increased as pH of the system increased. The three adsorbents surface charge density decreased as the pH of the system increased, with which the adsorption results showed agreement. This implied that the decreasing adsorption as pH increased could be due to the increasing amount of the OH^- **(Figure 18).**

The adsorption of Cr(VI) was increased from 13 to 60% in TBFZ3, as pH increased from 3.9 to 7.9. In TB, pH produced also a similar trend, but to a lesser extent. A higher pH from 3.7 to 7.7 also promoted the removal of Mo(VI) in TB and TBFZ3 systems, being 37.6% to 60.7% and 9.12% to 31.17%, respectively.

It was also worth mentioning that unlike metal cations, none of the four oxyanions formed any precipitate in the tested pH range of 3.6 to 7.9, which provided a great advantage in experimental manipulations.

3.5 The adsorption kinetics

The purpose of kinetic adsorption experiments was to estimate the rate of adsorption (removal) reaction and identify the reaction time required for adsorption to reach equilibrium. This information is crucial for application purposes and important for determining the how much time is needed in the studies of adsorption capacities and model fittings.

The adsorption kinetics is expressed by removal efficiency (%), which is calculated based on the following equation:

$$\text{The removal efficiency (\%)} = [(C_{initi} - C_t)/C_{initi}.] * 100 \qquad (3.5.1)$$

where $C_{initi.}$ and C_t stands for the concentrations of a given element at time 0 and time t (mg/L) in the aqueous phase, respectively.

In the different media (deionized water and the Vale Tailing Pond Water) are depicted in **Figures 19 & 21**.

3.5.1 The adsorption kinetics of oxyanions in deionized water

Deionized water was first used in the studies of adsorption kinetics. The adsorption kinetics of Se(IV), As(V), Mo(VI) and Cr(VI) on the SLG, TB, and TBFZ3 were investigated. A compromised pH for all oxyanions was chosen (7.00 – 7.50) in this set of experiment based on the previous pH effect studied where we have observed that (1) As (V) adsorption was not affected in a wide pH range; (2), a neutral pH was more favourable to adsorption for Cr(VI) and Mo(VI); (3) a neutral pH was unfavorable for Se(IV) adsorption, particularly on TB.

As predicted, in the selected experimental pH range, the removal of Se(IV) by TB and TBFZ3 was poor (practically zero in TB and 13% in TBFZ3) and slow at the chosen pH range, however Se(IV) removal by SLG reached nearly 80% after 7hours. The adsorption of other oxyanions increased slowly with time in the three tested materials. Cr(VI) adsorption was not ideal in all three materials in general, with a maximum removal of 63% in TBFZ3. For Mo(VI), the best material was TBFZ3, followed by TB and SLG. The adsorption of Mo by TBFZ3 appeared instantaneous and complete, followed by TB. The adsorption of Mo by SLG was poor.

Considering As(V) in SLG, a 99.7% removal was reached in 2h, which was confirmed as the most effective adsorbent for As(V). In TBFZ3, 82% of As(V) was removed in 7 hours, compared to 60% by TB in the same time period.

Although none of the three materials were ideal for Cr and Mo at the current pH, it is clear that TBFZ3 is better than non-modified TB. SLG is obviously much better a material for Se than TB and TBFZ3. The As removal was most effective by SLG and somewhat less efficient by TBFZ3 and TB which further confirmed the observation on pH effect studies where it showed that at pH around neutral the removal efficiency will be significantly affected in TB and TBFZ3 system. Regardless whichever oxyanion considered, TBFZ3 performs better than TB.

It is worth noting that the experiments were performed in triplicate, which provided the robustness of our observations and conclusions.

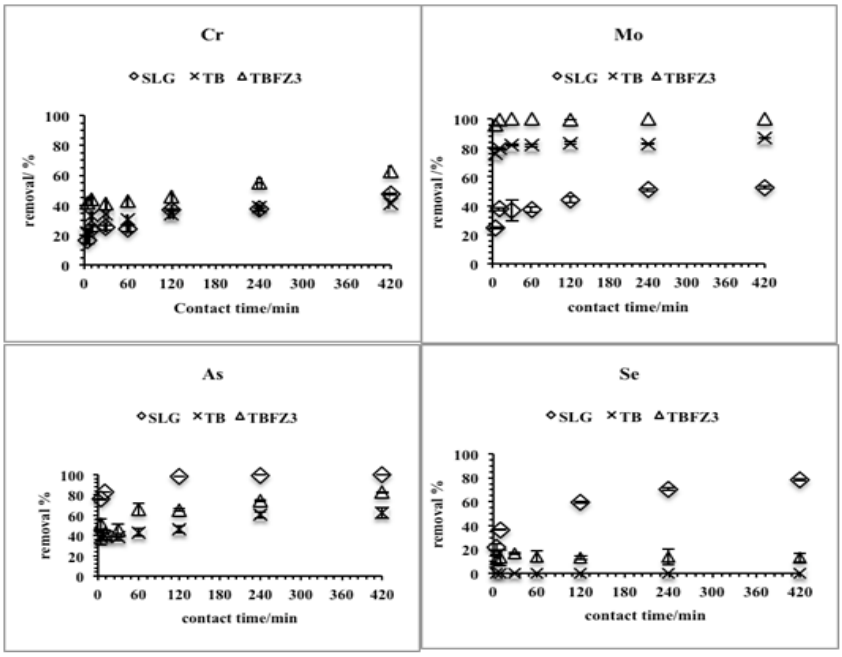

Figure 19 Kinetics test on 0.5000g of adsorbent immersed in 50.00mL of the mixed solution (Se(IV), As(V), Mo(VI) and Cr(VI)) of 50.0mg/L each in DW (T=22±2℃, pH controlled at 7.15 ± 0.19, 7.45 ± 0.35 and 7.31 ± 0.34 for SLG, TB and TBFZ3, respectively; with a constant shaking at 120 rpm).

Figure 19 shows that SLG was not an effective adsorbent for either Cr (VI) or Mo(VI). For the former, in the pH range of 3.7 - 7.7, the removal varied between 45 to 48%; whereas for Mo (VI), increasing pH from 3.7 to 7.7 and enhanced the removal from 9.0 to 37%.

3.5.2 The adsorption kinetics of oxyanions in Vale Tailing Pond Water

It is known that the adsorption reaction is also influenced by the initial concentration of adsorbate and other conditions such as electrolyte, temperature, etc. To estimate the adsorption kinetics of elements in a real situation, the studies were also conducted in a waste milling water collected from high sulphur containing tailing pond.

Ideally, it is desirable to study the kinetic of adsorption in original TPW, the extremely low concentrations of the interested oxyanions made it impossible (**Table 11**). In this set of experiment, the studies were carried out with the TPW spiked with a mixed anion solution of 1.00mg/L and 50.0mg/L each **(Figure 19 and Figure 20)**. The pH was adjusted to 7.25±0.25 and temperature at 22.0±2℃.In the TPW spiked with 1.00mg/L anion each, the adsorption of As(V) was almost immediate compared to a gradual completion in deionized water. It was also noted that the efficiency of the three tested adsorbents was equally great for As(V); even after the first 10min, only 1~5μg/L of As(V) remained in the TPW. In DW matrix, the adsorption efficiency of As(V) on TB and TBFZ3 were significantly lower (62 and 82% at 2h) compared to that of 99% on SLG (**Figure 19**).

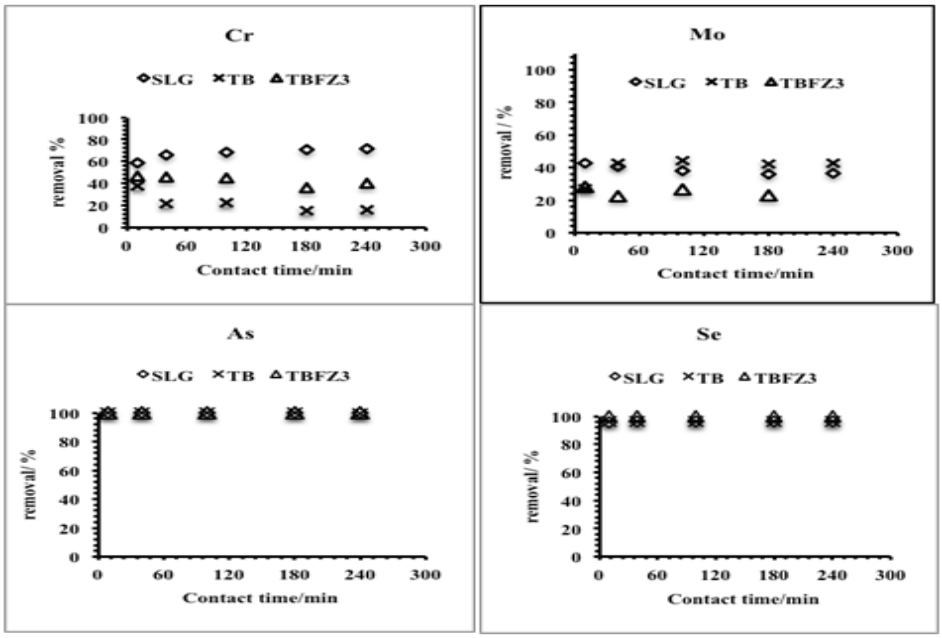

Figure 20 The adsorption kinetics of oxyanions on 0.5000g of adsorbent immersed in 50.0mL of TPWspiked with mixed anions of 1.0㎎/L each. (T=22±2℃, pH:7.22 ± 0.03, 7.09 ± 0.13 and 7.08 ± 0.27 for SLG, TB and TBFZ3 respectively; constantly shaking at 120 rpm).

Unlike the tests done with deionized water, where the adsorption of Se(IV) on TB and TBFZ3 was almost zero, the adsorption Se(IV) was almost instantaneous like As, and

did not demonstrate any difference among three adsorbents. The completeness of adsorption to Se was lower than to As and was close to 94~96%, representing a 44, 42 and 67μg/L of Se (IV) remaining in the aqueous phase in SLG, TB and TBFZ3, respectively after 4 hours of contact.

In the TPW, the adsorption of Cr(VI) was noticeably better for SLG than for the fly ash, and between TBFZ3 and TB the former was again better than the latter. There was also a noticeable drop of removal extend with time for TBFZ3 and TB. This could be due to the gradual replacement of CrO_4^{2-} by SO_4^{2-} in the TPW during the studying time. The gradual increase of removal % of Cr(VI) on SLG suggests a different adsorption mechanism for Cr(VI) on these two categories of materials.

Contrary to what was found in deionized water where nearly 83% and 100% of Mo(VI) was removed by TB and TBFZ3 after 4hours of contact, the adsorption of Mo was generally lower on three materials in the TPW compared to in deionized water.

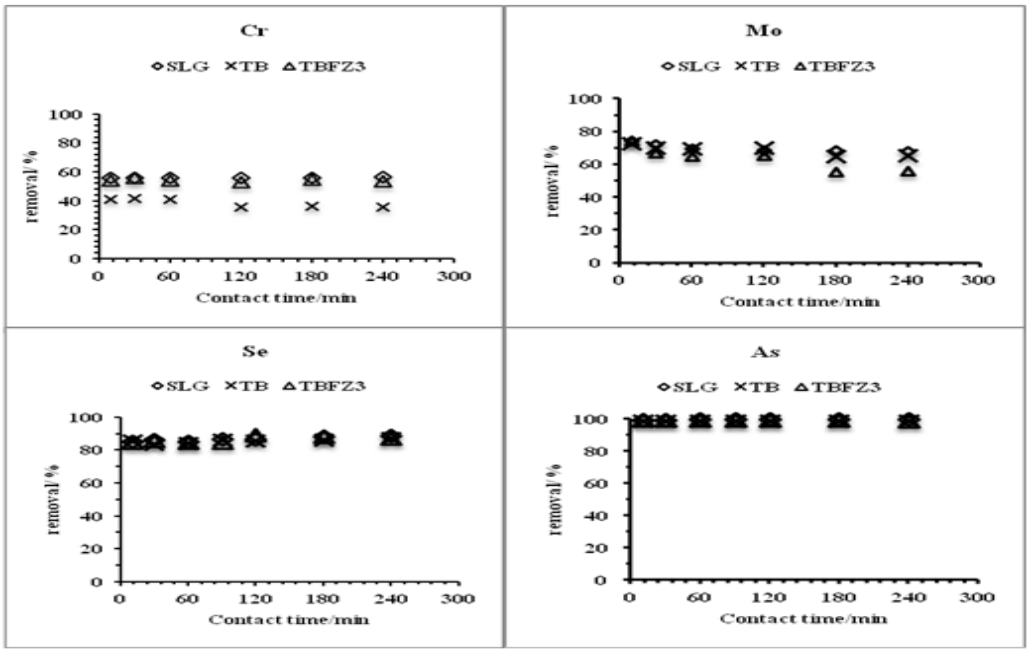

Figure 21 The adsorption kinetics of oxyanions on 0.5000g of adsorbent immersed in 50.00mL of TPW spiked with a mixed anions of 50.00mg/L each (T=22±2℃, pH: 7.42±0.16,7.43±0.13 and7.15±0.15 for SLG, TB and TBFZ3 respectively, constantly shaking at 120 rpm).

The adsorption behavior of As(V) and Se(IV) in 50.0mg/L spiked solution was similar that in 1.0 µg/mL. After 4hours of adsorption, about 80, 470 and 420µg/L of As(V) remained in the systems containing SLG, TB and TBFZ3, respectively, whereas for Se (IV), these values were 5.46, 6.32 and 6.40mg/L, respectively.

In 50.0mg/L spiked system, the relative removal percentage of Cr(VI) and Mo(VI) increased compared to that in 1.0mg/L spiked system; however, the elements remaining in solutions were very high, at 22.0, 32.7 and 23.7mg/L for Cr(VI) and 17.6, 19.1 and 24.2mg/L of Mo(VI) in SLG, TB and TBFZ3 systems, respectively.

In conclusion, SLG is the most effective material for As(V) removal in both DW and TPW. The adsorption kinetics is fast even in relatively low initial concentrations. In addition, thanks to a wide range of pH applicability of SLG, this material is ideal for the remediation of water contaminated by As(V). Fly ash materials TB and TBFZ3 are also suitable for As(V) removal though with lower efficiency. SLG can remove a great majority of Se(IV) from the solutions, but still a significant amount of Se(IV) remained in the solution, thus it is less effective. A low pH is more favourable for Se removal in all three materials. The adsorption kinetics of both As and Se was greatly enhanced in the TPW, probably due to the effect of electrolyte in such a water. None of SLG, TB or TBFZ3 can be used effectively for water remediation of Cr(VI) and Mo(VI) because of the incompleteness of the adsorption process in the tested pH conditions. It is also noticed that the adsorption kinetics and completeness of Cr and Mo were enhanced when the initial concentrations of these two adsorbates increased; which confirmed the importance of kinetic study under a realistic concentration. Even though fly ash is not ideal material for Cr and Mo removal, the modified fly ash has consistently demonstrated a better adsorption kinetic property for all tested anions.

3.6 Adsorption capacity of the adsorbent materials

Adsorption capacity is a key parameter for each adsorbent material. The adsorption capacity (mg/g) is the maximum amount of the molecule adsorbed (the adsorbate) per unit mass of the adsorbent. Experimentally, the adsorption capacity of an adsorbent can be obtained from the plateau of a plot of q_e vs. C_e where qe and Ce are the values of

amount of adsorbate retained by adsorbent and the concentration of adsorbate in aqueous phase at equilibrium under given initial concentration of the adsorbate in question. In this thesis, the experimental adsorption capacities of the adsorbents for the selected anions were investigated in deionized water and the TPW. The equilibrium time and pH of the studied system for each anion was determined based on previous kinetic and pH effect studies.

3.6.1 The adsorption capacity of the materials in deionized water

From the experimental data, it is seen that as the initial concentration of an oxyanion increased (C_e increases accordingly), q_e increased in general, until a plateau is reached, where q_e will not increase with the initial concentration. The q_e at this point will be the experimental adsorption capacity of a given material (**Figure 22 and 23**).

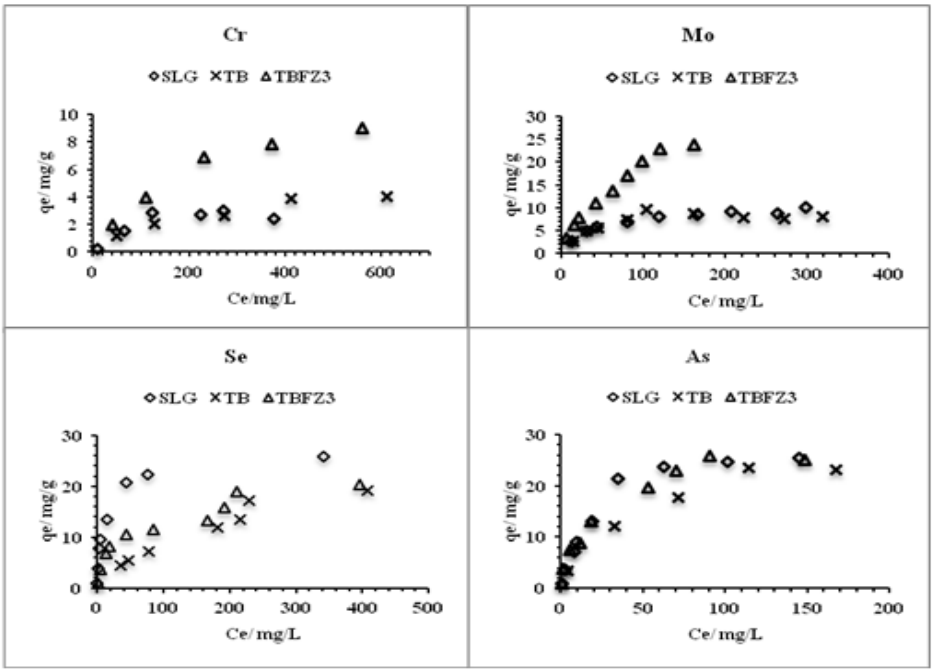

Figure 22 Adsorption isotherms of oxyanions in deionized water (0.5000g adsorbent,, T=22±2℃,equilibrium time =4 hours under constant shaking at 120 rpm. pH controlled at 5.3±0.3 for Se(IV) 7.25±0.25, for As(V), Cr(IV) and Mo (VI), respectively).

In deionized water, the adsorption capacities of all three tested materials for As(V) were all very similar and were significantly higher than to Cr(VI). The SLG adsorption capacity for Se was very close to that of As(V), whereas the adsorption capacities of TB and TBFZ3 for Se(IV) were remarkably lower. As for Mo(VI), the adsorption capacity of modified fly-ash was more than 2 times higher than that of SLG and TB. The adsorption capacities of the adsorbents for all studied oxyanions are given in **Table 13**.

Table 13 Summary of the experimental adsorption capacity of different materials to oxyanions (q_e) spiked in deionized water, expressed in mg or mmole of adsorbate per gram of adsorbent.

spl ID	Unit	As(V)	Se(IV)	Cr(VI)	Mo(VI)
SLG	mg/g	24.9	>26.4	3.1	10.2
	mmole/g	0.332	0.329	0.060	0.106
TB	mg/g	23.6	>18.9	3.4	8.2
	mmole/g	0.315	0.239	0.065	0.085
TBFZ3	mg/g	26	>17.2	8.5	23.8
	mmole/g	0.347	0.218	0.163	0.248

3.6.2 The adsorption capacities of the materials in the TPW

It was noticed that, when the experiments were conducted in the TPW, not only the adsorption kinetics were accelerated, the adsorption capacities of oxyanions were also remarkably increased, in general by 16% to 60% for Se(IV) and As(V), 2.5 to 3.0 times for Mo(VI), except in the TB system. The most striking increase was with Cr(VI), where 11.6, 10.4 and 4.2 times of increase were observed on SLG, TB and TBFZ3, respectively**(Figure 23 &Table 14).**

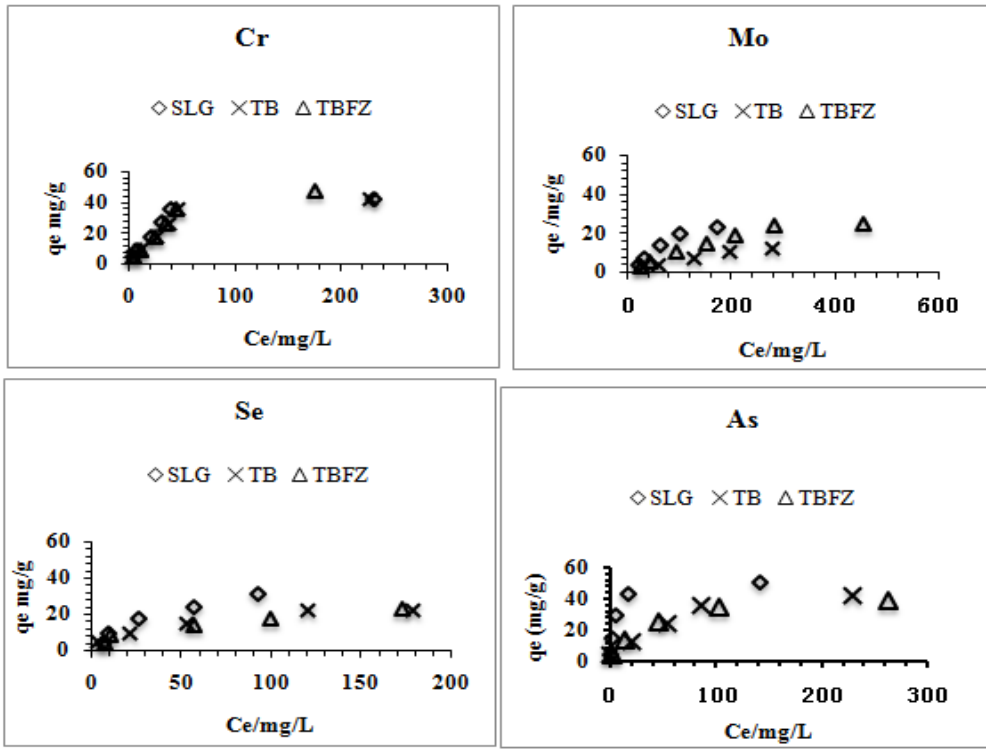

Figure 23 Equilibrium isotherms of each element with 0.5000g each adsorbent in Vale Tailing Pond Water, T=22±2℃ , t=4 hours. For As(V), Cr(IV) and Mo(VI), pH was controlled at 7.14±0.06, 7.21±0.11 and 7.23±0.11; for Se(IV), pH was controlled at 5.14±0.08; constant shaking at 120 rpm.

Table 14 Summary of experimental adsorption capacity of oxyanions on testing materials in the TPW

spl ID	Unit	As(V)	Se(IV)	Cr(VI)	Mo(VI)
SLG	mg/g	39.7	30.7	36.0	26.2
	mmole/g	0.530	0.329	6.924	0.274
TB	mg/g	23.6	>18.9	3.4	8.2
	mmole/g	0.392	0.239	0.682	0.255
TBFZ3	mg/g	26	>17.2	8.5	23.8
	mmole/g	0.521	0.288	0.684	0.225

3.6.3 Adsorption isotherms

The sorption curves or isotherms are very important to obtain information about the theoretic adsorption capacity of adsorbents and understand the mechanism of adsorption. The widely used isotherm equations for evaluating the adsorption equilibrium are Langmuir and Freundlich isotherms. The Langmuir isotherm is obtained under the assumptions that all sites are identical (homogeneous system), the adsorption can only occurs on definite number of sites and each of these sites can only adsorb one molecule, which consequently forms single layer of adsorbed molecules. It is further assumed that no interaction occurred between adsorbed molecules and these molecules cannot interact with adjacent sites [115]. The transformed linear Langmuir isotherm is used to fit the adsorption data in this study and is expressed as equation (1):

$$C_e/q_e = 1/(q_m * K_L) + C_e/q_m \quad \text{or} \quad C_e/q_e = K_a + C_e/q_m \qquad (1)$$

where C_e (mg/L) is the equilibrium concentration of adsorbate in solution at a given initial concentration, q_e (mg/g) is the amount of adsorbate adsorbed on adsorbents at equilibrium of above system, and q_m and K_L are the maximum monolayer adsorption capacity (mg/g) and the binding constant or Langmuir adsorption constant (L/mg) which can be obtained from the fitting curve of equation 3.8.1, respectively.

The Freundlich isotherm, based on Langmuir isotherm, is an empirical equation which extended its application to heterogeneous systems and is represented as equation (2):

$$\log q_e = \log K_F + (1/n) \log C_e \qquad (2)$$

where K_F and n are indicative of the extent of the adsorption and the adsorption intensity, respectively.

The adsorption capacity at equilibrium q_e (mg/g) can be calculated from the experimental data, is defined as the mass of adsorbed element per mass of adsorbent:

$$q_e = [(C_{init.} - C_e) * V]/m \qquad (3)$$

where q_e defined as before, V is the volume of the aqueous phase of the studied system (L), m is the mass of studied adsorbent (g). $C_{initi.}$ is the initial concentration of the adsorbate (mg/L), and C_e is the concentration of the adsorbate in aqueous phase at equilibrium.

In all the studies, the temperature of adsorption system was controlled at 22 ± 2^oC.

The data of **Figures 22&23** were used in the Langmuir and Freundlich adsorption isotherm model fittings.

3.6.4 The adsorption isotherm of oxyanions spiked in deionized water

The parameters obtained from the two isotherm model fittings are given in **Table 15**. The experimental data in deionized water fit relatively well to both Langmuir and Freundlich adsorption isotherms for Se(IV),As(V),Mo(VI) and Cr(VI) on all tested adsorbents. It can be seen from correlation coefficient (R^2) that generally the data fitted Langmuir model better than Freundlich model. The agreement of the Langmuir model with the experimental results suggests that a monolayer coverage of Se(IV),As(V),Mo(VI) and Cr(VI) on the outer surface of adsorbent SLG, TB and TBFZ3. The apparent equilibrium constant [116] ($K_a=1/(q_m* KL)$ determined by the product of KL and q_m can be used as relative indicators of the affinity of adsorbent towards adsorbate. It is high K_a suggests a lower affinity. In this case, the affinity of adsorbent SLG, TB and TBFZ3 for Cr(VI) is much lower in comparison with Se(IV),As(V) and Mo(VI).

Table 15 Langmuir and Freundlich fitting parameters for Se(IV), As(V), Mo(VI) and Cr(VI)in deionized water

Langmuir Parameters in DW

	R^2			K_L (L/mg)			$q_{m\ calc.}$ (mg/g)			K_a [or $1/(q_m*K_L)$]		
	SLG	**TB**	**TBFZ3**	**SLG**	**TB**	**TBFZ3**	**SLG**	**TB**	**TBFZ3**	**SLG**	**TB**	**TBFZ3**
Se(IV)	0.99869	0.92563	0.95656	26.56	28.28	21.69	26.53	26.18	20.75	0.3635	6.4863	1.845
As(V)	0.99196	0.98254	0.98346	29.13	29.25	28.4	28.9	28.74	27.93	0.5862	1.2631	0.535
Mo(VI)	0.98764	0.98445	0.94631	10.89	8.73	35.1	10.76	8.59	33.22	3.4871	1.6955	1.988
Cr(VI)	0.9171	0.95912	0.99397	3.5	5.59	12.58	3.21	5.36	12.5	17.809	37.563	16.81

Freundlich parameters in DW

	R^2			$\log K_f$(mg/g)			1/n		
	SLG	**TB**	**TBFZ3**	**SLG**	**TB**	**TBFZ3**	**SLG**	**TB**	**TBFZ3**
Se(IV)	0.93338	0.99351	0.93759	0.5222	0.408	0.2107	1.82	1.50	2.22
As(V)	0.96338	0.98463	0.94352	0.3379	0.2479	0.4244	1.77	1.88	1.98
Mo(VI)	0.94658	**0.74384**	0.99242	0.1375	0.2084	0.1099	2.80	3.20	1.70
Cr(VI)	**0.89525**	0.97846	0.97646	0.5222	0.7558	0.5923	1.82	2.01	1.72

3.6.5 The adsorption isotherm of oxyanions in the TPW

Table 16 shows the fitting parameters of Langmuir and Freundlich adsorption isotherm for Se(IV), As(V), Mo(VI) and Cr(VI) on sludge(SGL), fly ash(TB) and TBFZ3 in the Vale Tailing Pond Water. Correlation coefficient (R^2) shows again that the data generally fit better on Langmuir model Freundlich model, except for Mo(VI).The three adsorbents show a good lineal relationship (all the correlation coefficients are above 0.9) except for Mo(VI).

Comparing the three adsorbents, sludge exhibited a higher adsorption capacity for As(V) and Se(IV) than TB and TBFZ3. The difference was attributed to the large surface area and the presence of Al_2O_3 and iron oxides (Fe_2O_3) of sludge in the previous study. The adsorption isotherms were better fitted with the Langmuir isotherm equation (**Table 15**).**Table 13** shows the maximum Mo(VI) uptake onto the TBFZ. That is the surface area of TBFZ3 is 10 times higher than TB. On the other hand, the significant amounts of crystalline/amorphous minerals of TBFZ3.

A comparison of experimental q_m and calculated q_m indicates that the adsorption capacity in TPW was greater than in DW (Table 16); however, both experimental q_m were lower than calculated $q_{m.}$ TPW contained higher amount of Na, Ca, Fe, Cu and anions (Cl^-, SO_4^{2-}), which potentially influence each adsorbent on the concentrations of Se(IV), As(V), Mo(VI) and Cr(VI). It was observed that when MoO_4^{2-} was at 1ppm spiked in the TPW, the color of the solution became blue. This observation only occurred in preparing solutions with TPW, which was immediately right after collecting water sample. The spiked Mo may have formed a complex with the chemical present in the water and the new Mo compound could be less favorable for adsorption on TBFZ3 and TB.

In fact, TPW contains high concentrations of electrolytes compare to DW. After having collected the TPW sample, there were no particles at the beginning. However, there were some precipitates (iron oxide or iron hydroxide) as time went on. Iron oxide or iron hydroxide is a great adsorbent, which can adsorb Cu^{2+}. There will be more and more Cu^{2+} captured by the iron precipitates. Therefore, the solutions with TPW did not become blue after a period of time.

On the other hand the adsorption of Mo increased as the solution was more alkaline. This sorption of MoO_4^{2-} can be attributed to the fact that both the TPW acidity and the hydrolysis of oxyanions are strongly pH related. Molybdate can be held on surfaces of hydrous oxides at pH values below the isoelectric points for the solution. According to Davis and Kent [114], the isoelectric points for most Al- and Fe- hydrous oxides are in the range of 7.3 to 9.1, which are higher than the effluent pH values for the spiked solution interaction experiments. Binding of molybdate onto reactive Fe hydrous oxides to form ferric molybdate ($Fe_2(MoO_4)_3.8H_20$), which has a very low solubility, might cause Mo precipitation. It suggests that Mo was most strongly adsorbed on hydrous ferric oxides [116].

Table 16 Comparison of experimental and calculated q_m

	DW						TPW					
	$q_{m\ calc.}$ (mg/g)			$q_{m\ calc.}$ (mg/g)			$q_{m\ calc.}$ (mg/g)			$q_{m\ exp}$ (mg/g)		
	SLG	**TB**	**TBFZ3**	**SLG**	**TB**	**TBFZ3**	**SLG**	**TB**	**TBFZ3**	**SLG**	**TB**	**TBFZ3**
Se(IV)	26.53	26.18	20.75	25.90	19.20	20.34	46.30	25.97	26.04	30.74	22.14	22.73
As(V)	28.9	28.74	27.93	25.55	23.59	25.21	52.08	48.54	42.02	50.77	42.08	38.60
Mo()	10.76	8.59	33.22	10.20	8.15	23.84	64.10	20.70	44.05	22.80	12.00	24.50
Cr(V)	3.21	5.36	12.5	3.06	4.03	9.06	47.62	50.25	62.50	42.06	42.43	47.49

Table 17 Langmuir and Freundlich parameters for Se(IV), As(V), Mo(VI) and Cr(VI) adsorption on adsorbents SLG, TB and TBFZ3 in TPW

Langmuir Parameters in the TPW

	R^2			K_L (L/mg)			$q_{m\ calc.}$ (mg/g)			K_a[or $1/(q_m*K_L)$]		
	SLG	**TB**	**TBFZ3**	**SLG**	**TB**	**TBFZ3**	**SLG**	**TB**	**TBFZ3**	**SLG**	**TB**	**TBFZ3**
Se(IV)	0.95395	0.97583	0.96487	0.02	0.04	0.05	46.30	25.97	26.04	1.0291	1.1462	1.394
As(V)	0.99968	0.95775	0.99551	0.00	0.02	0.01	52.08	48.54	42.02	0.0682	0.7788	0.564
Mo(V)	**0.57301**	0.92369	0.90477	0.07	0.49	0.16	64.10	20.70	44.05	4.2469	10.051	6.956
Cr(VI)	0.99048	0.98328	0.96596	0.01	0.02	0.02	47.62	50.25	62.50	0.5914	0.7676	0.938

Freundlich parameters in Tailing pond water

	R^2			$\log K_f$(mg/g)			1/n		
	SLG	TB	TBFZ3	SLG	TB	TBFZ3	SLG	TB	TBFZ3
Se(IV)	0.9416	0.98666	0.90399	0.2255	0.455	0.3532	1.50	2.46	2.21
As(V)	0.90611	0.97096	0.97454	1.0643	0.6113	0.6212	2.72	2.26	2.31
Mo(VI)	0.94375	0.98959	0.95767	0.5053	0.4956	0.5451	1.14	1.55	1.30
Cr(VI)	**0.85689**	**0.89001**	0.93308	0.4847	0.3902	0.323	1.80	1.69	1.52

Chapter 4 Conclusion

This research project was composed of two parts – the chemical characterization and determination of the adsorption properties of the selected adsorbents sludge (SLG) and fly-ash, pristine (TB) and modified (TBFZ3), towards 4 oxyanions in both deionized water and TPW. The studies included the pH effect, the adsorption kinetics as well as the adsorption isotherms describing their adsorption capacity on the three adsorbents.

TB, TBFZ3 and SLG had average particle sizes of 179.79, 114.77 and 54.22μm, respectively. SLG presented a significantly high surface area compared to non-modified fly ash TB. The surface of modified fly ash (TBFZ3) was around 5 times higher than pristine fly ash. The cation exchange capacity (CEC) of the three tested materials SLG, TB and TBFZ3 were 55.03, 3.32 and 15.45meq/g, respectively and SLG showed again an enhanced surface property of TBFZ3 over TB. The particle size of all three absorbents greatly influenced the adsorption rate, a decrease in particle size leading to an increase in surface area and consequently a higher adsorption potential and an adsorption capacities. In general we observed an order of surface adsorption capacity of SLG >TBFZ3> TB.

The acidic and alkaline properties of original and modified materials in deionized water and in the presence of a mixed adsorbates solution have been examined. In deionized water, SLG appeared acidic and pH of the aqueous phase slightly dropped from 5.58 to 5.23 in 2 hours of contact. Fly-ash samples with or without modification, were alkaline in aqueous solutions and constant in pH, usually at 11.3±0.5 over 4 hours. The pH control during the studies is much less crucial in the studies involving oxyanions than metal cations, due to the simple reason that oxyanions do not normally form precipitates in a large tested pH range. In the studies with oxyanions, it was found that, in SLG, solution pH appeared to not affecting Cr(VI) and As(V) adsorption, promoting slightly Mo(VI), but slightly demoting Se(VI) adsorption as pH increased. The adsorption of Mo(VI) by SLG was the lowest among the 4 tested oxyanions. In TB and TBFZ3, adsorption of Cr(VI), Mo(VI) and Se(VI) was generally poor and that of Cr(VI) and

Mo(VI) increased with pH. Se(VI) adsorption decreased sharply with pH increase.

The adsorption kinetics of adsorbents to oxyanions spiked in deionized water was done in a cocktail solution of 50.00mg/L each at a controlled pH of 7.3±0.3. It was found that SLG had a fastest adsorption rate for As(V), where 97.0% of the 50μg/mL solution was gone from the aqueous phase within 120min; it was followed by Se(IV) where 78.0% was gone after 420min. SLG removed only 41.0 % of Cr(VI) and 52.7% of Mo(VI) in 420min. Non-modified Thunder Bay fly-ash (TB) did not adsorb any Se(IV) at all at this pH (not favorable for Se adsorption), but adsorbed Cr(VI) at 41.0%, Mo(VI) at 52.7% and As(V) at 63.2% after 420min. Compared to TB, TBFZ3 was more effective in removing Cr(VI), Mo(VI) and As(V), and they were 62.7, 11.0 and 99.8% in 420min, respectively. In the TPW, the adsorption kinetics and completeness of As and Se on three tested materials have been remarkably increased, particularly for Se on fly ash of TB and TBFZ3 from almost zero to 100% in few minutes. The influence of matrix on Cr and Mo has been mixed and also dependent on the initial concentrations of adsorbates, usually increased with C_e. This indicates that both the matrix of adsorbing system and the nature of oxyanions are extremely important factors that will affect the adsorption processes.

In the studies on the adsorption capacity of materials to oxyanions spiked in deionized water, the pH was controlled at 5.3±0.3 for Se(IV), as the adsorption decreased rapidly as pH passed this value. For As(V), Cr(VI) and Mo(VI), pH was controlled at 7.25±0.25 respectively as at this range, pH either did not remarkably affect adsorption for As(V), or enhanced it for Cr and Mo. A close to neutral pH was chosen in the study to have a better representation of a natural aquatic system. SLG adsorbed effectively Se(IV) and As(V)(26.53mg/g and 28.9 mg/g, the value of experimental q_m), but poorly to Cr(VI) and Mo(VI)(10.76mg/g and 3.12mg/g). TBFZ3 adsorbed As as efficiently as SLG, but for Se it was less effective than SLG. However, TBFZ3 adsorbed Mo(VI) and Cr(VI)better than SLG. Non-modified TB is the least effective adsorbent among the three materials.

In conclusion, SLG is the most effective material for As removal from both DW and TPW. Moreover, due to a wide range of pH applicability of SLG and a high equilibrium constant **(**T=22±2℃, t= 4 hours**)** between solid and aqueous phase, this material is ideal

for the remediation of water contaminated by As(V). TB and TBFZ3 are equally satisfactory materials for As removal. The above three materials can also remove a large majority of Se from the testing solutions, but they are less efficient than for As . Although under testing conditions SLG, TB andTBFZ3 can be all remove some Cr and Mo, their efficiencies are so low that they are not considered as valuable materials for Cr and Mo removal. A much effective removal of Mo (in a cocktail solution of 50.0mg/L each) by TBFZ3 and TB in DW has a difference from those in 1.0mg/L and 50.0mg/L cocktail solutions of the TPW. The mechanisms of Mo adsorption in these systems need to be studied further.

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